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RESEARCH ON SPUTTERING OF FERROELECTRIC THIN FILMS

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R. Neurgaonkar
Principal Investigator

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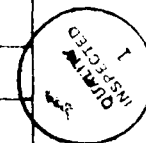
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1.0 PROGRESS SUMMARY

This report covers work on sputtered ferroelectric thin films carried out over the period of April 15, 1986, to December 31, 1989, in the Ferroelectric Materials Department of the Rockwell International Science Center under Contract No. F49620-86-C-0052. This report covers the progress for the entire period of the three-year program. During this period, significant progress has been made in the growth of thin films of tungsten bronze $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (PBN:60), $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$ (SBN:75), and perovskite PLZT.

The goals of this program required the installation and modification of thin film growth and characterization equipments, including magnetron sputtering units and techniques for measuring temperature-dependent dielectric and polarization properties. A hot-stage was added to our MRC sputtering units to maintain substrate temperatures in the range of 600-700°C. This allowed us to achieve single crystal or grain-oriented ferroelectric thin films during the deposition step, and thus eliminated the need for post-annealing of these films which often degrades the film quality. Measurements on these ferroelectric thin films were pushed down to film thickness of 0.5 μm . The input from these measurements has been instrumental in the development of high quality ferroelectric thin films.

The advantages of ferroelectric thin films for optoelectric applications have not been fully exploited due to the difficulties of achieving single crystal films of adequate quality. Isolated examples of successful growth have been reported on such materials as LiNbO_3 and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ (SBN:50) for optical waveguides and surface acoustic wave applications using liquid phase epitaxial (LPE) techniques. Based on work reported in the literature, LPE growth is suitable for only lattice-matched substrate materials, and in some instances, film quality is a severe problem due to the inclusion of solvents. For this reason, the magnetron sputtering technique has been used extensively to explore simple, as well as complex, ferroelectrics based on Pb^{2+} -containing solid solutions.

Two important ferroelectric compositions, tungsten bronze PBN:60 and perovskite PLZT have been selected in the present study. We selected PBN:60 because it appears close to the morphotropic phase boundary (MPB) and possesses an exceptionally

large longitudinal electro-optic coefficient ($r_{51} = 2300 \times 10^{-12}$ m/V) with very large polarization ($\geq 70 \mu\text{coul/cm}^2$). The PLZT composition selected in the present study also exhibits a large electro-optic coefficient ($r_{51} > 1000 \times 10^{-12}$ m/V) with large polarization ($\sim 45 \mu\text{coul/cm}^2$).

The growth of tungsten bronze thin films has been highly successful using various substrates such as SBN and Si. At present, the growth of PBN:60 has been studied in three different orientations of SBN, e.g., (001), (100) and (110), with great success and this is the first time these films are available for device studies. Orthorhombic and tetragonal tungsten bronze forms are related to each other in the following way:

$$(110)_{\text{tetra}} = (100)_{\text{ortho}}$$

Although the growth of PBN:60 has been successful on the (110)-oriented SBN:60 substrates, we believe that both the tetragonal and orthorhombic forms coexist in this orientation. However, at present, it is not known how to stabilize these forms independently with respect to this orientation. Further study is underway to determine structural stability with respect to temperature and other growth conditions.

We have also been successful in growing PLZT thin films in both polycrystalline and single crystal form using various substrates. For example, when glass, or quartz were used as substrates, the films were polycrystalline and showed the pyrochlore phase below 600°C . On the other hand, films grown on SBN:60 substrates were single crystal and we did not observe the pyrochlore phase at any growth temperature. This is a unique advantage for developing single crystal PLZT films, and we believe that this is the first time PLZT single crystal thin films have been produced on tungsten bronze substrates. The availability of these films should make a significant impact on various device applications such as spatial light modulators (SLM), guide wave optics, pyroelectric detectors and SAW.

Both PBN:60 and PLZT thin films have been successfully grown on (100)-oriented Si substrates. The PBN:60 films grown at elevated substrate temperatures showed considerable grain-orientation with remanent polarization above $7 \mu\text{coul/cm}^2$. We believe that with further improvement in grain-orientation and fine tuning of the film composition, it should be possible to attain high polarization and large electro-optic

effects in these films. For electronic memory applications, one needs film thicknesses down to 1000\AA , whereas for spatial light modulators (SLMs), the film thickness should be $5\text{ }\mu\text{m}$ or more. Currently, we have grown these films in thicknesses of 0.5 to $5.0\text{ }\mu\text{m}$ without any major problems. In the case of PLZT thin films, however, film peeling was occasionally observed when the film thickness was over $5\text{ }\mu\text{m}$.

We anticipate a great future for these films in various electronic device applications, particularly electronic memories and SLMs.

As a result of this three-year effort, several technical papers have been prepared, with two already submitted for publication. This report includes drafts of these papers.



1.0 PROGRESS SUMMARY

This report covers work on sputtered ferroelectric thin films carried out over the period of May 1, 1987, to December 31, 1989, in the Ferroelectric Materials Department of the Rockwell International Science Center under Contract No. F49620-86-C-0052. The period covered by this report is the second year of this three-year program. During this period, significant progress has been made in the growth of thin films of tungsten bronze $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (PBN:60), $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$ (SBN:75), and perovskite PLZT.

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We anticipate a great future for these films in various electronic device applications, particularly electronic memories and SLMs.

As a result of this three-year effort, several technical papers have been prepared, with two already submitted for publication. This report includes drafts of these papers.



EPITAXIAL GROWTH OF TUNGSTEN BRONZE PBN:60 THIN FILMS FOR OPTICAL APPLICATIONS

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ABSTRACT

Tungsten bronze ferroelectric $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (PBN:60) single crystal thin films have been grown by the sputtering technique on (001), (100), and (100)-oriented SBN:60 substrates. The crystallinity and quality of these PBN:60 films were found to depend upon the substrate lattice-mismatch, temperature and annealing conditions. Although good-quality films were grown for all three substrate orientations, the highest quality films were generally produced on (100)-oriented SBN:60 substrates due to a closer lattice match and a slower rate of film crystallization. The films deposited on Pt-metallized SBN also exhibited good grain orientation for thickness up to $8\text{ }\mu\text{m}$ with room temperature dielectric constants near 1700.

INTRODUCTION

The use of ferroelectric thin films for optoelectronic applications is being actively pursued by researchers in the U.S.¹⁻⁵ and elsewhere.⁶⁻¹⁰ Currently, LiNbO_3 and LiTaO_3 are actively used for guided wave optics, modulators, surface acoustic wave (SAW) and nonlinear optical applications due to their good optical quality and crystal large size. Although other electro-optic materials, such as KDP, ADP, KTN, $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}\text{BaTiO}_3$ and $\text{BaNaNb}_5\text{O}_{15}$, have been utilized in these applications, they have not found widespread acceptance due to crystal size restrictions in some cases and material properties in others.



We have studied the growth techniques for several tungsten bronze crystals whose characteristics are substantially better than LiNbO_3 . Although crystals like $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ have proven to be effective in various applications, including guided wave optics,¹¹ streak cameras,¹² and photorefractive applications,¹³⁻¹⁵ the higher figure-of-merit tungsten bronzes based on Pb^{2+} -containing compositions are difficult to grow in optical quality due to the loss of Pb^{2+} during crystal growth. Since these Pb^{2+} -containing bronzes have substantially higher figures-of-merit than SBN, in this work, we have produced single crystal PBN:60 thin films using the magnetron sputtering technique. The results of this work are discussed in this paper.

BACKGROUND ON TUNGSTEN BRONZE PBN:60

Ferroelectric tungsten bronze oxides have been studied for their electro-optic and pyroelectric properties and have been found to be effective for many related applications. The bronze compositions can be represented by the general formulae as $(\text{A}_1)_4(\text{A}_2)_2\text{C}_4\text{B}_{10}\text{O}_{30}$ and $(\text{A}_1)_4(\text{A}_2)_2\text{B}_{10}\text{O}_{30}$, in which A_1 , A_2 , C and B are 15-, 12-, 9- and 6-fold coordinated sites in the crystal lattice structure. The tetragonal bronze prototypic structure is shown in Fig. 1 in projection on the (001) plane. A wide range of solid solutions can be obtained by substituting different A_1 , A_2 and B cations, and a number of different types of ferroelectric and ferroelastic phases have been identified (over 100 compounds and solid solutions). The ferroelectric phases can be divided into two groups: those with tetragonal symmetry (4 mm), which are ferroelectric, and those with orthorhombic symmetry (2 mm), which are both ferroelectric and ferroelastic.

Table I summarizes the current best tungsten bronze compositions for optical and nonlinear optical applications. Since the figures-of-merit for optical and photo-



refractive applications are taken as r_{ij}/ϵ , $n^3 r_{ij}$ and $n^3 r_{ij}/\epsilon$, respectively, it is important that one examine bronzes exhibiting large electro-optic coefficients, and at the same time be relatively easy to grow in thin film form. Based on our work in this family, we have found the tetragonal bronze compositions to be promising, and several of these compositions have been grown in our laboratory as well as in Japan. Of the total group of tetragonal bronzes, the SBN and PBN solid solutions have been selected in the present work. SBN solid solution crystals exhibit a strong transverse (r_{33}) electro-optic coefficient, whereas strong longitudinal (r_{51}) and transverse (r_{33}) electro-optic coefficients have been observed for PBN crystals. The phase relation and crystal growth problems associated with each system are discussed below, together with the potential optical interest in each.

Figure 2 shows the ferroelectric tungsten bronze system $\text{Pb}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ in which the MPB region is located at $x = 0.37$. In this region, the electro-optic, pyroelectric, piezoelectric and dielectric properties are large and are nearly temperature-independent. As shown in Fig. 2, on a binary phase diagram an MPB appears as a nearly vertical line separating two ferroelectric phases, i.e., the boundary occurs at a nearly constant composition over a wide temperature range up to the Curie temperature. Poled crystals near such a boundary show unique and enhanced electro-optic properties because of the proximity in free energy of an alternative ferroelectric structure. A detailed description of MPB behavior has been provided by Jaffe et al.¹⁶

In the $\text{Pb}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ system, Shrout et al.¹⁷ demonstrated that it is possible to grow striated, small size crystals with compositions close to the MPB. For compositions on both sides of the boundary, the g_{ij} quadratic electro-optic coefficients are largely temperature-independent, as expected, and are significantly larger than those for $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ solid solution crystals. With increasing Pb^{2+} content, the piezoelectric



coefficients d_{15} and d_{33} , shown in Fig. 3, escalate dramatically as the composition approaches the MPB, with longitudinal values larger than those found for BaTiO_3 .

Two phases exist in tungsten bronze $\text{Pb}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$: orthorhombic (2 mm) for $x \leq 0.37$ and tetragonal (4 mm) for $x > 0.37$. Since the tetragonal composition $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (PBT:60) is close to the MPB, this composition was selected for thin film growth. As summarized in Table 1, this near-morphotropic composition has a dielectric constant $\epsilon_{11} = 1900$ and an electro-optic coefficient $r_{51} = 2400 \times 10^{-12}$ m/V at room temperature based on previous bulk single crystal measurements.

Experimental Procedure

The proper preparation of sputtering targets of 3 to 6 in. diameter is important to achieve compositional homogeneity in ferroelectric films. The use of a binder in the starting materials and careful sintering helped to prepare large-size targets of the appropriate thickness, with high purity carbonates and oxides used as starting materials. The cold-pressed disks were carefully sintered in an oxygen atmosphere above 1200°C and the target compositions were checked by x-ray diffraction measurements.

Single crystals of SBN:60 and BSKNN grown by the Czochralski technique were used as substrate materials, along with other materials such as sapphire, quartz and glass. In the case of SBN:60 crystals, wafers as large as 1 in. diameter were available for this work. Since tungsten bronze single crystals exhibit natural facets, the orientation of a given crystal, e.g., (001), (100) and (110), was easily achieved.

As shown in Fig. 4, a magnetron sputtering unit was used for film growth. To obtain single crystal or grain-oriented films, it was important that the substrate be at elevated temperatures, preferably around 600°C . As shown in Fig. 4, a substrate hot-stage was incorporated so that the substrate temperature could be changed according to



observed film crystallinity and orientation, both of which are influenced by temperature. After evacuation of the chamber to 5×10^{-5} Torr, either argon or argon + oxygen were used for sputtered film growth.

RESULTS AND DISCUSSION

The growth of tungsten bronze composition $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (PBN:60) was studied using various substrates under different conditions. Since PBN:60 does not exhibit a high symmetry pyrochlore structure as observed in perovskite compositions such as PbTiO_3 and PLZT, the development of PBN:60 films with a tungsten bronze structure, was greatly simplified. The qualitative results of our experiments are summarized in Table 2.

Table 2
Ferroelectric PBN:60 and SNB:75 Films

SBN:60 Substrates	Nonferroelectric Substrates (MgO, Si, Quartz, Glass)
<u>Substrate Temperature < 300°C:</u>	<u>Substrate Temperature < 300°C:</u>
Poorly crystallized Needed annealing over > 500°C	Amorphous films up to 500°C
<u>Substrate Temperature > 600°C:</u>	<u>Substrate Temperature > 600°C:</u>
Well crystallized films	Well crystallized films for anneals over 800°C
Single crystal films	Polycrystalline films
Excellent surface quality	Good surface quality
Ferroelectric	Ferroelectric



Thin Film Growth on SBN:60 Substrates

Figure 5 shows x-ray diffraction patterns of PBN:60 thin films deposited on (001), (100) and (110)-oriented tungsten bronze SBN:60 substrates using a single target. The growth of these films was successful in all orientations and showed the typical tungsten bronze structure, except for a few extra weak reflections for films grown on (110) substrates. As can be seen from these figures, the epitaxy is generally good and the films are well crystallized. When the films were deposited on (001)-oriented SBN:60 substrates, only the (001) and (002) x-ray diffraction peaks were observed, whereas the reflections corresponding to (400), (600) and (800) were observed when the films were deposited on (100)-oriented SBN:60 substrates. In the case of (110) SBN:60 substrates, lines corresponding to (330), (440) and (660) were dominant and we also found additional reflections in close agreement with the (400) and (600) diffraction peaks. This indicates that orthorhombic (100)-oriented films are present. The tungsten bronze compositions exhibit two structural forms, tetragonal (4 mm) and orthorhombic (2 mm), and they are crystallographically related to one another as follows:

$$\sqrt{2} \cdot a_{\text{Tetra}}(\text{i.e. } [110]) = a_{\text{ortho}}[100] .$$

This suggests that films deposited on (110)-oriented substrates are metastable and can take either a tetragonal or orthorhombic form. However, the current results are not sufficient to predict under what conditions one form is stable over another. Currently, further experiments using varied substrate temperatures are underway to study the structural transformation behavior on (110) substrates. Recently, Adachi et al demonstrated the growth of tetragonal $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ (KLN) on the $a/\sqrt{2}$ substrate, but did not mention orthorhombic KLN on (001) or (100)-oriented substrates. Based on our current work, it seems possible to stabilize either the tetragonal and orthorhombic forms using (110)-oriented tetragonal substrates and appropriate growth conditions.

The rate of deposition of various orientations was checked and it was found that the crystallization rate is faster along $\langle 001 \rangle$, an observation consistent with our work on bulk single crystals of these compositions which grow only along $\langle 001 \rangle$. As shown in Fig. 6, the intensity of the film peaks was found to increase with film thickness. Based on our LPE work on SBN and LiNbO_3 films, it is important to have film thickness 8 μm or higher to suppress contributions from the substrate. However, except



for spatial light modulators (SLM), we believe that thicker films are not required for device studies.

The lattice constants established for PBN:60 films using x-ray diffraction data are $a = 12.503\text{\AA}$ and $c = 3.986\text{\AA}$, in close agreement with the target values. This clearly suggests that the film and target compositions are almost the same.

To measure the dielectric properties, it is necessary to use an intermediate metallic layer like Pt or Au between the film and substrate. Since gold and lead form an alloy, we used Pt in this work; an approximately 1000\AA -thick Pt layer was deposited prior to PBN:60 thin film growth. The films were grown on both heated and cold substrates with similar results. Figure 7 shows that the grain orientation in the PBN:60 films has been retained for all thicknesses. However, film orientation becomes a problem when the film thickness exceeds $8\text{--}10\text{ }\mu\text{m}$. We have also deposited perovskite PLZT thin films on Pt/SBN substrates with good success, but in this case, the maintenance of grain orientation for films thicker than over $3\text{--}5\text{ }\mu\text{m}$ was a problem. Currently, we are also exploring other electrodes that will match with the SBN substrates and selected thin films.

The dielectric properties for one PBN:60 film grown on a (001)-oriented SBN:60 substrate are shown as a function of temperature and frequency in Fig. 8. The dielectric anomaly at 370°C indicates the ferroelectric transition; this temperature is nearly 100° higher than found in small single crystals of this composition, suggesting that film stress may be altering the transition temperature. The film composition may also be altered somewhat from the target composition, although the general good agreement in lattice constants indicates that the difference is probably small. It is noteworthy that the dielectric anomaly, which has the characteristic features of polar c-axis behavior, progressively diminishes at higher frequencies. It is suspected that this also results from film stress, resulting in clamped behavior at frequencies approaching 100 kHz or above.

Because of the Pt substrate metallization required for these measurements, the film shown in Fig. 7 is not fully oriented. As a result, the dielectric data represent effects from both polar and nonpolar directions and thus show a gradual rise in the dielectric constant below 150° due to nonpolar contributions to the permittivity. Nevertheless, this rise is slight, so that at room temperature, the dielectric constant is 1700, only slightly above the value at 150°C . This dielectric value compares well with



small bulk single crystal values, and does not appear to change appreciably with film thicknesses down to $1.0\ \mu\text{m}$.

CONCLUSIONS

We have successfully demonstrated the sputtered epitaxial growth of near-morphotropic tungsten bronze PBN:60 thin films on SBN:60 single crystal substrates. Although the growth process needs to be further refined before these films can be considered for practical applications, particularly in optics, it is evident that the absence of a pyrochlore phase greatly contributes to the relative ease with which PBN:60 films can be grown with good film morphology. It appears in this work that a significant factor for further film improvements lies with the crystalline quality, surface polish, and the lattice match of the underlying substrate. The combination of PBN:60 films with SBN:60 substrates provides a very good lattice match, and particularly a large refractive index difference (2.32 for PBN vs 2.24 for SBN) which is necessary for guided wave optical applications.

The comparative ease with which PBN may be grown on SBN suggests using PBN film compositions as an intermediate layer between the underlying substrate and other ferroelectric film compositions, perhaps including those in the perovskite family (e.g., PZT/PLZT). Such a structure could include several film layers of differing composition, as illustrated in Fig. 9. An attractive feature of such a structure is the very large refractive indices possible in many perovskite materials (2.40 to 2.76) which may otherwise be too difficult to grow in optical quality due to severe lattice mismatches with available substrate materials. In this regard, PBN can be very effective in achieving a lattice match since its lattice constants, as well as its symmetry, can be altered by simple changes in the Pb:Ba ratio.

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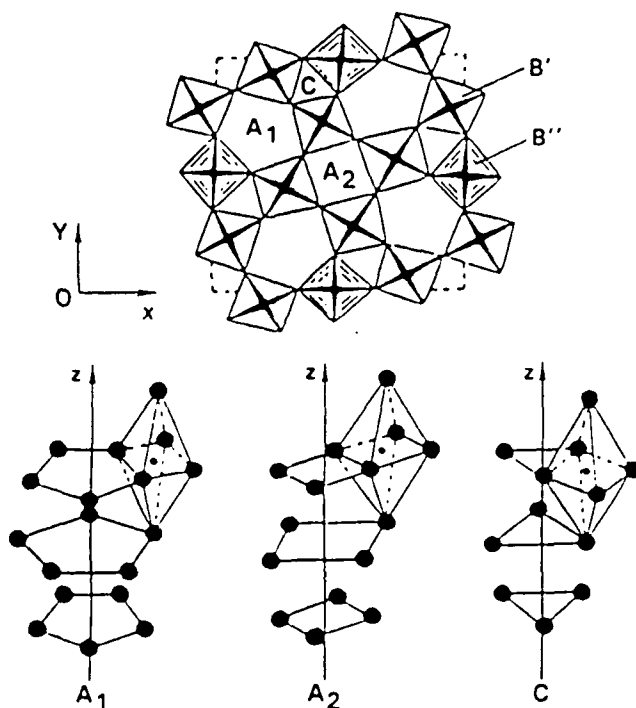
FIGURE CAPTIONS

- Fig. 1 Projection of the tetragonal tungsten bronze crystal structure on the (001) plane.
- Fig. 2 Curie temperatures vs composition diagram for the PbNb_2O_6 - BaNb_2O_6 binary system.
- Fig. 3 Piezoelectric d_{33} and d_{15} coefficients as a function of composition in the PbNb_2O_6 - BaNb_2O_6 system.
- Fig. 4 Schematic representation of the sputter coating process.
- Fig. 5 Tungsten bronze PBN:60 film on (001), (100) and (110)-oriented SBN:60 substrates.
- Fig. 6 Intensity as a function of film thickness for PBN:60 films.
- Fig. 7 Grain-oriented PBN:60 thin film on Pb/SBN:60 substrate.
- Fig. 8 Dielectric constant as a function of temperature for PBN:60 on SBN substrate.
- Fig. 9 Advantages of multilayer ferroelectric thin films.



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FIGURE 1



• CHEMICAL FORMULAE

$(A_1)_4(A_2)_2C_4B_{10}O_{30}$ = FILLED STRUCTURE

$(A_1)_4(A_2)_2B_{10}O_{30}$ = UNFILLED STRUCTURE

A₁ = 15-FOLD COORDINATED SITE

A₂ = 12-FOLD COORDINATED SITE

C = 9-FOLD COORDINATED SITE

B = 6-FOLD COORDINATED SITE (TWO SITES)

• CRYSTAL STRUCTURE

4/mmm TO 4mm (TETRAGONAL-TETRADONAL)

4m mm TO mm2 (TETRAGONAL-ORTHORHOMBIC)

• KNOWN SYSTEMS

150 COMPOUNDS OR MORE

SOLID SOLUTIONS BETWEEN END MEMBERS

SEVERAL MORPHOTROPIC PHASE BOUNDARY
SYSTEMS

• PROPERTIES

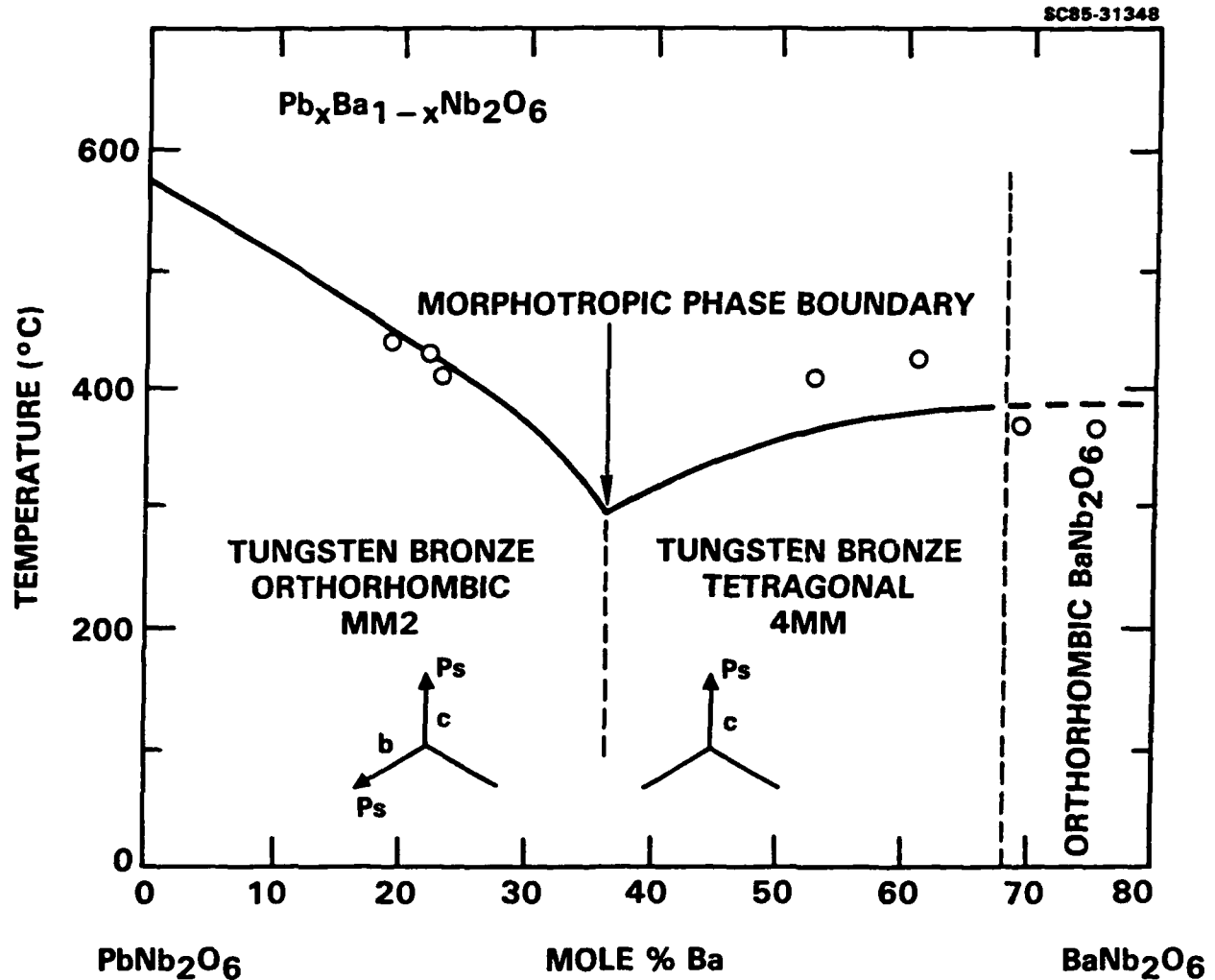
LARGE ELECTRO-OPTIC, PYROELECTRIC AND
PIEZOELECTRIC

COEFFICIENTS — DEPEND ON PROTOTYPIC PHASE



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FIGURE 2



THE PSEUDO-BINARY $\text{PbNb}_2\text{O}_6 - \text{BaNb}_2\text{O}_6$ SYSTEM



FIGURE 3

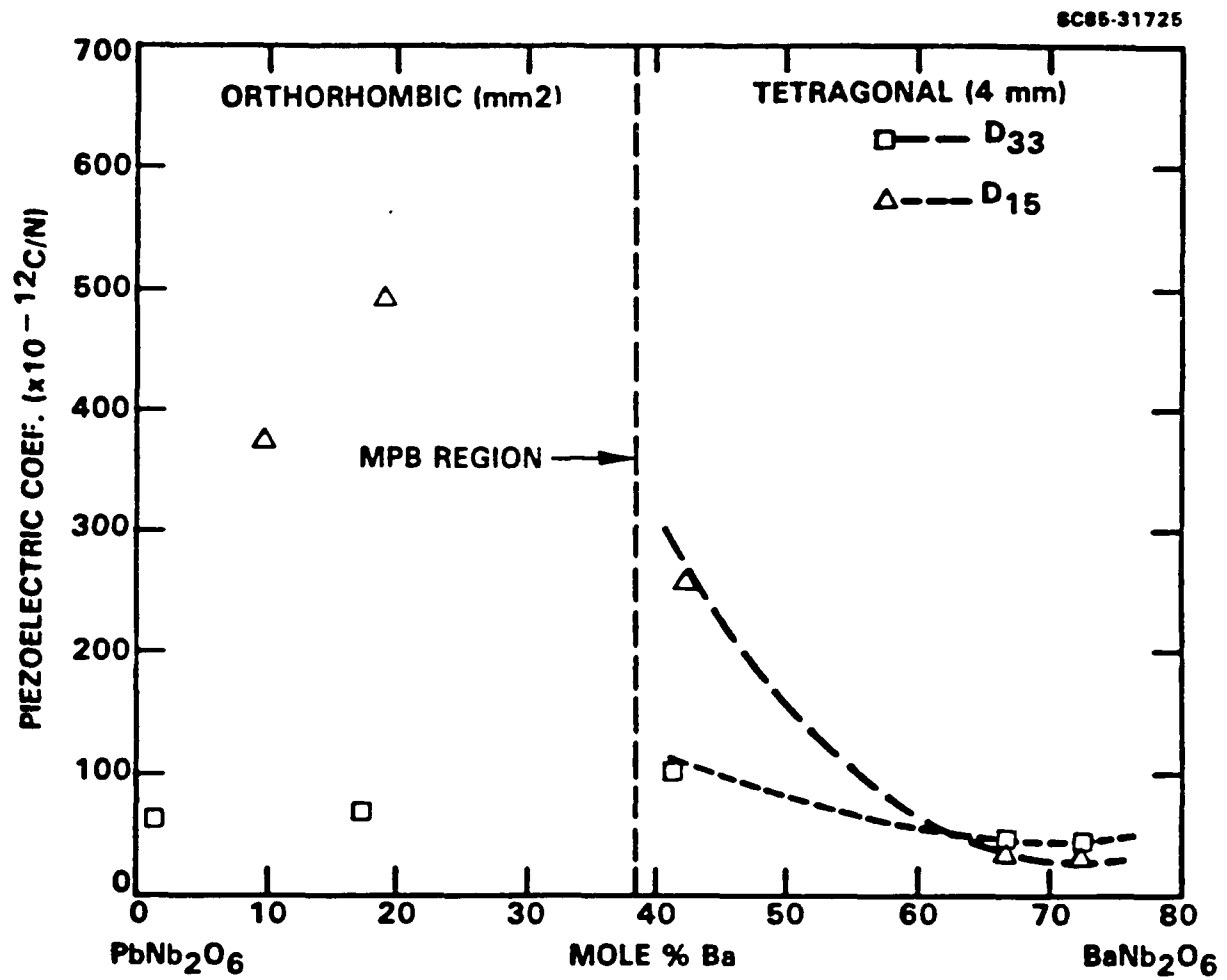
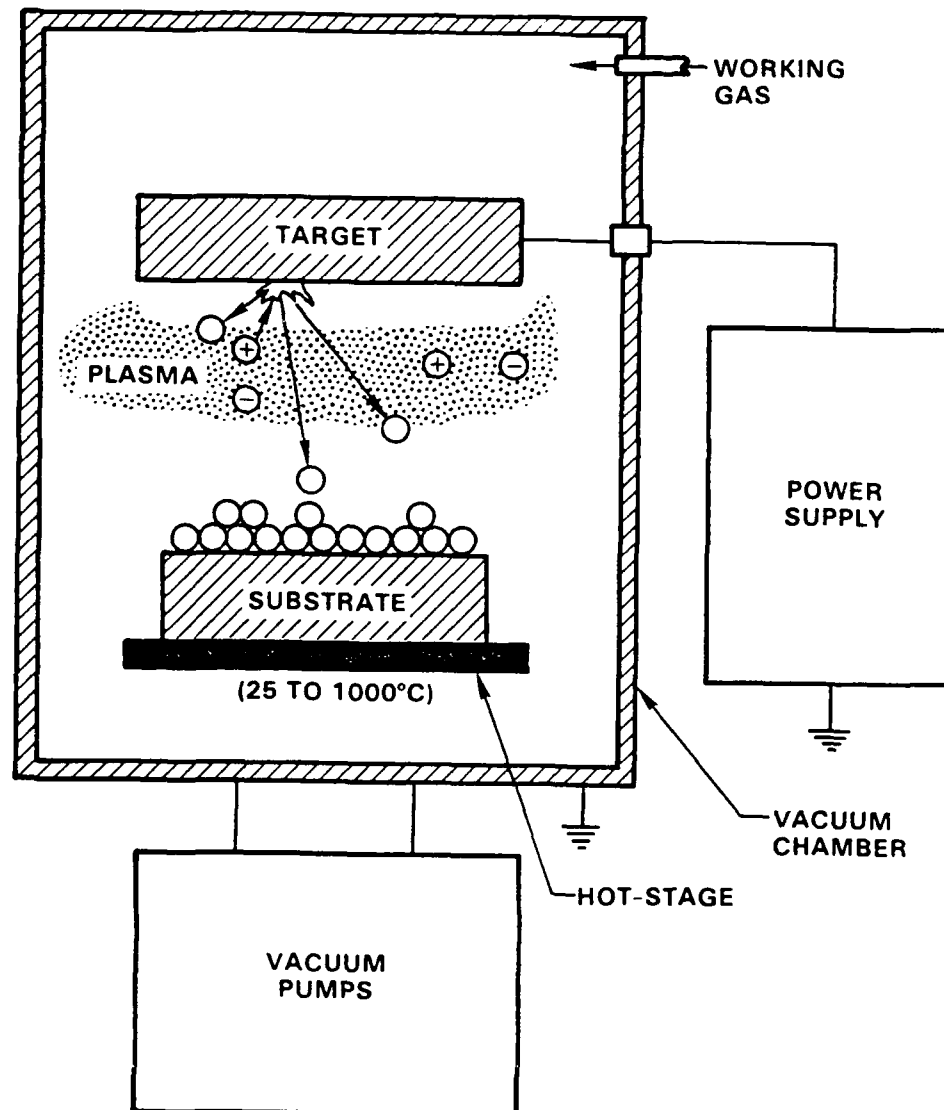




FIGURE 4





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FIGURE 5

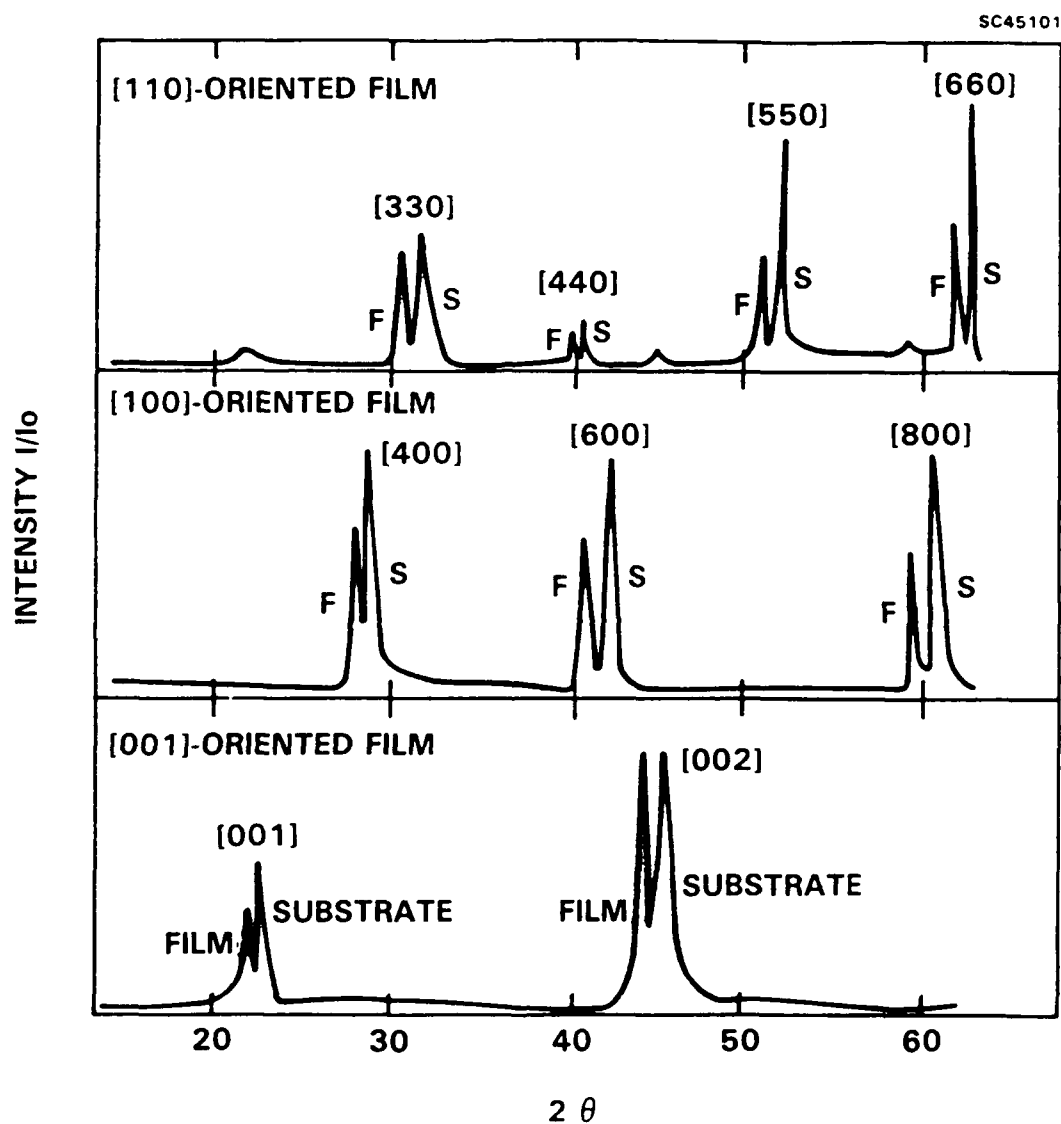




FIGURE 6

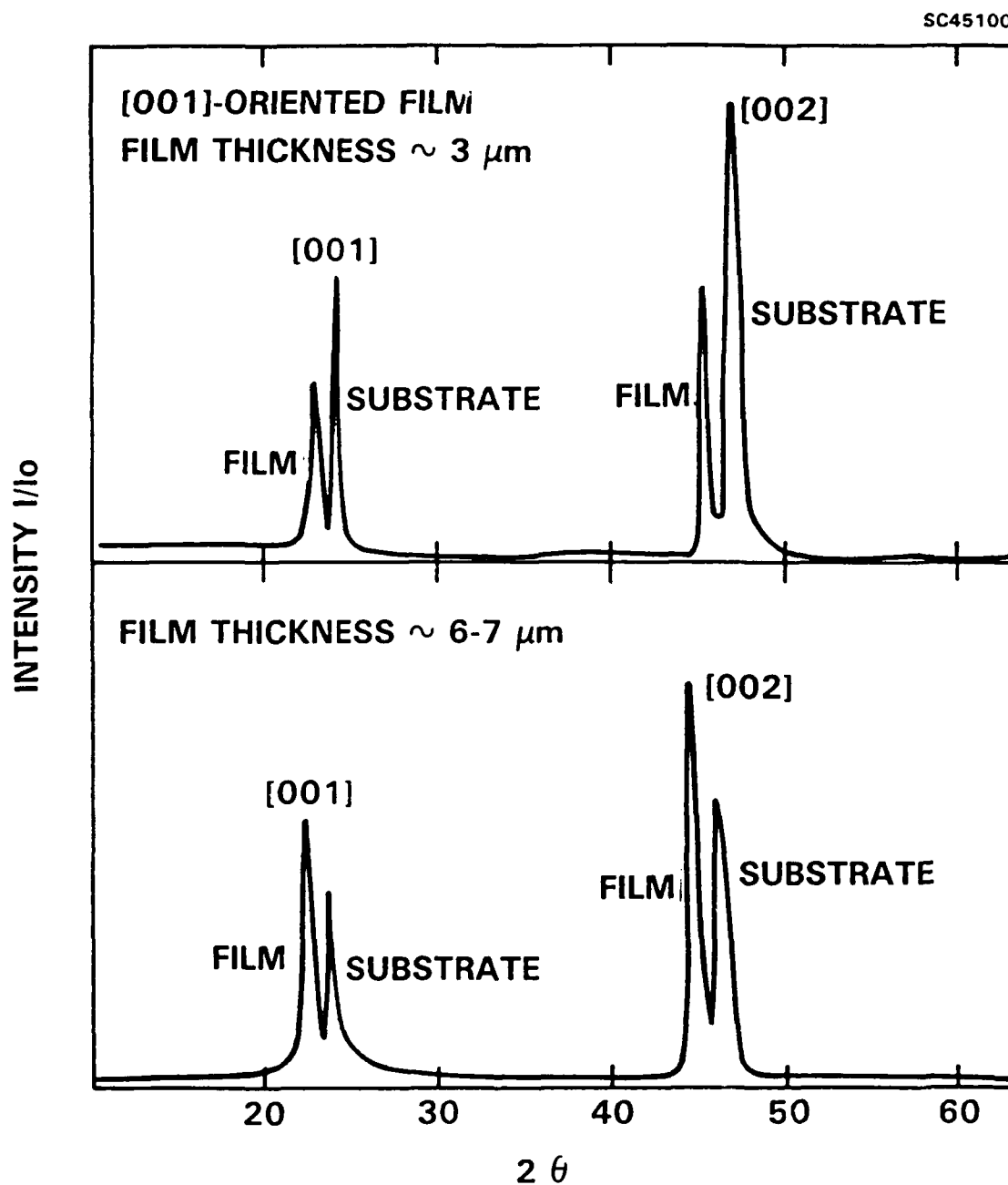




FIGURE 7

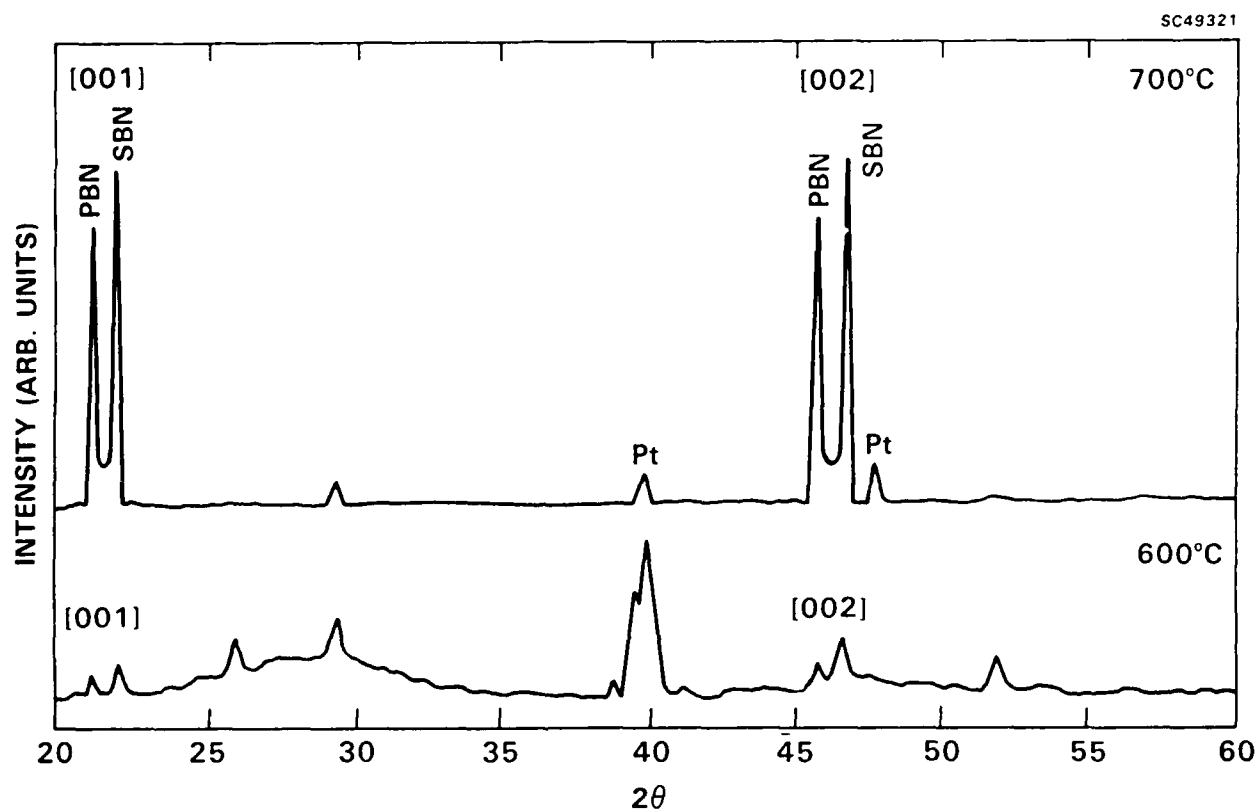




FIGURE 8

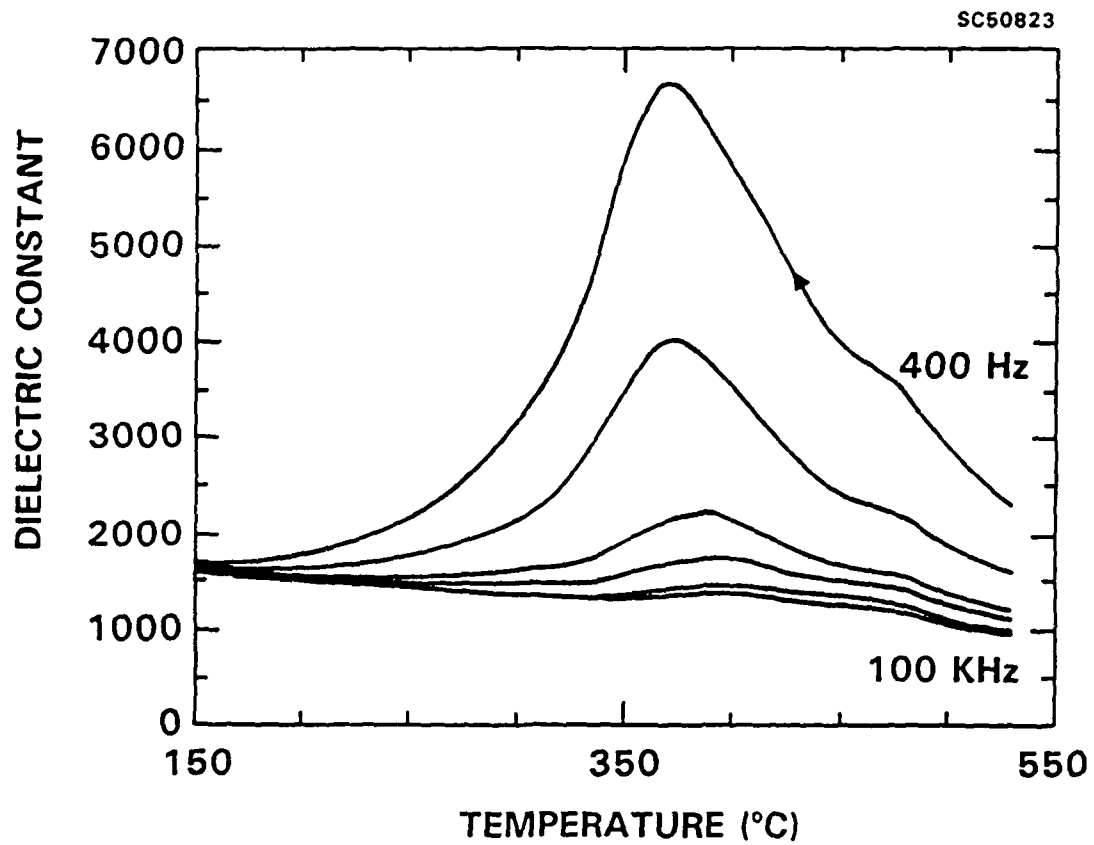
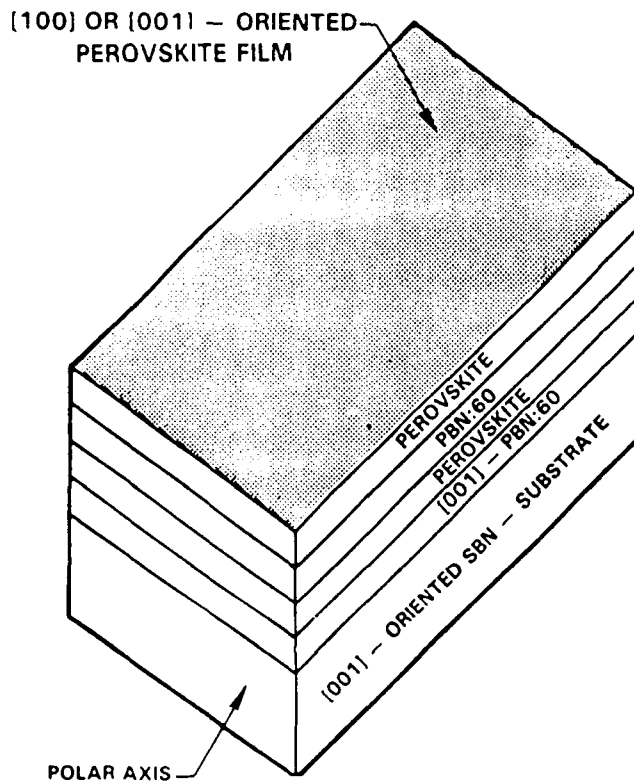




FIGURE 9



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<u>SBN:60</u>	<u>PBN:60</u>	<u>PEROVSKITES</u>
[001]	[001]	[100] OR [001]
$n = 2.24$	$n = 2.32$	$n = 2.4 \text{ TO } 2.76$
LARGE r_{33}, ϵ_{33}	LARGE r_{51}, ϵ_{11}	LARGE r_{51}, ϵ_{33}
$T_c = 78^\circ\text{C}$	$T_c = 280^\circ\text{C}$	$T_c = 100 - 300^\circ\text{C}$

PEROVSKITE FILMS

PZT, PLZT, PZNT, PBFT

APPLICATIONS

- OPTICAL WAVEGUIDES AND SWITCHES
- 3-D STORAGE AND DISPLAY
- PYROELECTRIC AND PIEZOELECTRIC
- MULTILAYER CAPACITORS



INTEGRATION OF TUNGSTEN BRONZE PBN:60 THIN FILMS WITH Si FOR ELECTRONIC MEMORY APPLICATIONS

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ABSTRACT

This paper reports preliminary results on the integration of ferroelectric tungsten bronze $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (PBN:60) thin films with semiconducting Si-substrates by the rf sputtering technique. The films were deposited primarily on (100)-oriented Si substrates at 300°C followed by a 600°C oxygen anneal. The films thus grown are grain oriented along the (001) direction with a spontaneous polarization of over $6 \mu\text{Coul}/\text{cm}^2$. With further improvements in film composition and quality, they could be suitable for both electronic memory and spatial light modulation applications.

INTRODUCTION

A basic characteristic of all ferroelectric materials for non-volatile memory applications is the hysteretic behavior relating the polarization P and applied field E_a (Fig. 1). There is a nominal threshold (or coercive field, E_c) above which the polarization changes sign. The two zero-field values, $\pm P_r$, are equally stable. Thus, no applied field or voltage is required to maintain the memory, which is why the device is termed "non-volatile". This bistable operation may be contrasted with the operation of memories such as nematic liquid crystal display devices, which relax back to a single favored state if the



applied voltage is interrupted, or with Si DRAM, which require a "refresh" voltage many times per second to maintain their storage information.

The materials requirements for electronic memories based on ferroelectric films are relatively modest; in particular, because most ferroelectric materials have a spontaneous polarization that corresponds to about 100 times the switched charge of an Si DRAM of the same area, it is not necessary to choose a ferroelectric material with a large polarization: 0.1 to 1.0 $\mu\text{coul}/\text{cm}^2$ is sufficient. This permits many non-oxide crystals to be considered as cell materials, in addition to the ABO_3 perovskites favored at present. Currently, perovskite PZT and PLZT films prepared by the sol-gel technique are being explored with significant success;¹ however, the technique has a limitation in that it cannot produce highly grain-oriented films. Noteworthy contributions on PZT and PLZT have been reported by various researchers: Nakagawa et al,² at Ramtron and TRW,³ Payne⁴ and Dey et al.⁵ These films have been tested successfully by Krysalis for ferroelectric RAMs.⁶

Besides PZT and PLZT, other equally important materials being explored for this application are $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and PBN:60. Currently, we have been investigating PBN:60 because it has high polarization and it does not exhibit a low temperature nonferroelectric pyrochlore phase. The development of these films at lower temperatures has resulted in well-oriented PBN:60 thin films on Si substrates. This paper reports the growth of these films and their future for electronic memories and SLMs.

EXPERIMENTAL PROCEDURE

The sputtering targets employed for film growth were comprised of a mixture of PbO, BaO and Nb_2O_5 . Approximately 5 mole% excess of PbO was added to maintain a



stoichiometric Pb^{2+} concentration in the films. To maintain uniform film thickness, we have been using 3" diameter targets; however, for larger area films, it may be necessary to use 6" diameter targets. The targets were prepared using ceramic sintering or hot-forging; well-mixed powders were cold pressed and then sintered or hot-forged at 1000-1200°C after ball-milling. The targets thus prepared showed no extra phases.

The PBN:60 thin films were deposited with an rf magnetron sputtering system; the sputtering conditions are summarized in Table 1. (100)-oriented Si substrates of dimensions $50 \times 50 \times 1$ mm and $25 \times 25 \times 1$ mm were used. Some of the substrates were polished to optical quality, etched with acid after polishing, or mechanically polished. Substrate temperatures were maintained between 100-300°C during these film growths. The films were then annealed above 550°C for 3-4 hrs in an oxygen atmosphere. X-ray diffraction and ferroelectric characterization techniques were employed to determine the crystallinity, grain orientation, and dielectric and polarization properties of these films.

RESULTS AND DISCUSSION

The $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ composition occurs close to the morphotropic phase boundary region as shown in Fig. 2, and it possesses exceptionally large dielectric, electro-optic and polarization properties. The highest polarization measured in PBN:60 single crystal is on the order of $70 \mu\text{coul}/\text{cm}^2$, which is significantly higher than the current best perovskite PLZT ceramics or thin films ($45 \mu\text{coul}/\text{cm}^2$). Furthermore, PBN:60 thin films are easier to grow than PLZT due to the absence of a low-temperature nonferroelectric pyrochlore phase.



As summarized in Table 1, all films were grown in an Ar:O₂ atmosphere. The sputtering conditions were as follows:

Target-Substrate Distance:	4-5 cm
Input Power Density:	1.9 to 2.4 W/cm ²
Gas Mixture:	Ar:O ₂ (50:50)
Substrate Temperature:	100 to 300°C
Deposition Rate:	~ 50-100Å/hr
Annealing Temperature:	~ 550-650°C

Figure 3 shows an x-ray diffraction pattern for a PBN:60 thin film deposited on (100)-oriented Si. The growth and annealing conditions seem to be favorable to induce complete grain orientation in ferroelectric PBN:60 thin films. For growths below 300°C substrate temperature, the films are essentially polycrystalline and required annealing above 600°C. Films grown above 400°C showed a few x-ray diffraction peaks which were too weak to be identified; however, annealing above 600°C produced grain-oriented films. Based on these observations, it is clear that if the films are deposited above 500°C, it may be possible to eliminate the post-growth annealing step. This could be advantageous since annealing often degrades the film surface quality.

At higher temperatures (> 600°C), oxidation of Si to SiO₂ is imminent. For this reason, it is important that growth be conducted at lower temperatures. In the present case, it is possible to carry out PBN:60 film growths near 500°C due to the absence of a pyrochlore phase. We are also exploring the compatibility of PBN:60 with Si as a function temperature.



The lattice-constant refinement of PBN:60 thin films indicates $c = 3.991\text{\AA}$, which is close to the target value (3.988\AA). However, we are studying the ferroelectric properties of these films as a function of the target composition to allow us to achieve the highest polarization and electro-optic coefficient in these films.

FILM THICKNESS

In real ferroelectrics, E_C depends strongly on the sample thickness, as first detailed by Callaby.⁷ For thick specimens, E_C varies as d^{-n} , where n is a number between $1/3$ and $1/2$; this weak-field theory was developed by Kay and Dunn⁸ and has been found to be valid for several materials, as shown by Scott et al.¹¹ However, for thinner samples or higher voltages, a rather different dependence sets in, with $n = 4/3$. This was first reported by Hadni and Thomas⁹ and is not completely understood.

This change in the thickness dependence of E_C in ferroelectrics occurs near a thickness of 200 nm and has a profound practical effect on device construction. When we multiple E_C by d to obtain V_S , we find that the dependence discussed above has two effects. It produces an optimum thickness near 250 nm, at which V_S is an absolute minimum (around 1.0 V); and it defines a processing window of film thicknesses (from about 100 to 800 nm), within which V_S will be less than the 5.0 V CMOS logic levels for Si ICs. Within this processing window, the devices will be faster near the thin limit of 100 nm; in fact, as shown by Stadler,¹¹ for a fixed 5.0 V driving voltage, the switching speed will vary as $d^{-3/2}$, so that a 100 nm film will be approximately eight times faster than a 400 nm film.

Currently, we have been growing PBN:60 thin films in the range of 0.5 to 5 μm without significant problems. As discussed above, the thinner films are required for



nonvolatile memories. Although we have not established the film thickness conditions for SLM applications, we suspect that those concepts require film thicknesses of 5-10 μm . In our current work, we have noticed that lower film thicknesses present few problems, but higher thickness films show several major problems:

1. Film peeling
2. Degradation of grain orientation
3. Film quality is still excellent, but it is a concern for thicker films.

FERROELECTRIC PROPERTIES

Measurements of the dielectric and polarization properties of the PBN:60 films were made using Pt metallization pads on the film surface and Pt substrate metallization, upon which the films were deposited, for electrical contact. Figure 4 shows the behavior of the weak-field dielectric constant at 1 kHz as a function of temperature for a 4 μm film. There are two very broad peaks in the dielectric constant, with the upper one centered near 270°C, which is consistent with the temperature expected for the ferroelectric phase transition in PBN:60, although the dielectric maximum is about an order of magnitude below what one would expect from a classical phase transition. This may be due to film stress, in which case the lower temperature dielectric peak may be an artifact of the stressed film. At room temperature, the dielectric constant is approximately 1300, and declines rapidly at lower temperatures in a manner consistent with orientation along the ferroelectric polar axis.

Measurements of the hysteretic behavior of film polarization with applied voltage were made with a modified Sawyer-Tower circuit driven by a variable-frequency



signal generator. Figure 5 shows the hysteresis curve for a 4 μm film at room temperature; this slim-loop behavior has been typical of the films we have grown thus far. The remanent polarization at zero bias, P_r , varied between 5-7 $\mu\text{coul}/\text{cm}^2$ at room temperature, whereas the saturation polarization at high fields (above 25 kV/cm) was generally above 15 $\mu\text{coul}/\text{cm}^2$. Both of these values are good, but we feel that the value of P_r in particular is presently far below what can be expected for a high-quality film.

An encouraging aspect of these PBN:60 thin films has been a low incidence of pinhole defects which would effectively short the sputtered Pt metallization pads to the underlying substrate metallization. Even in cases where an array of large-area (1.4 mm diameter) pads were used, very few pads (and occasionally, none at all) were found to be shorted, or show degraded dielectric behavior, for films down to 1.0 μm thickness. Considering the large contact diameters, this qualitatively indicates a low density of pinhole defects in these films, particularly when compared with sputtered PZT films we have grown which generally show a substantially higher incidence of shorted contacts.

CONCLUSIONS

The growth of grain-oriented tungsten bronze PBN:60 thin films has been successful on Si-substrates up to 5 μm thickness. The ferroelectric measurements indicate that the dielectric constant is over 1200 at room temperature with a spontaneous polarization exceeding 6 $\mu\text{coul}/\text{cm}^2$. Although this polarization is sufficient to test the RAM device concepts, improvement in film quality and properties will be necessary. This is the first time PBN:60 thin films have been produced for both electronic memories as well as for SLM applications. Because this material possesses an exceptionally large



longitudinal (r_{51}) electro-optic coefficient and potentially large polarization, these films will remain a prime candidate for future device consideration.

ACKNOWLEDGEMENT

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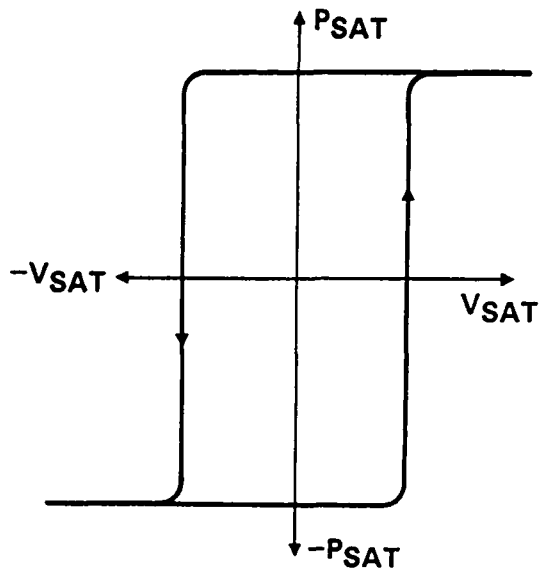
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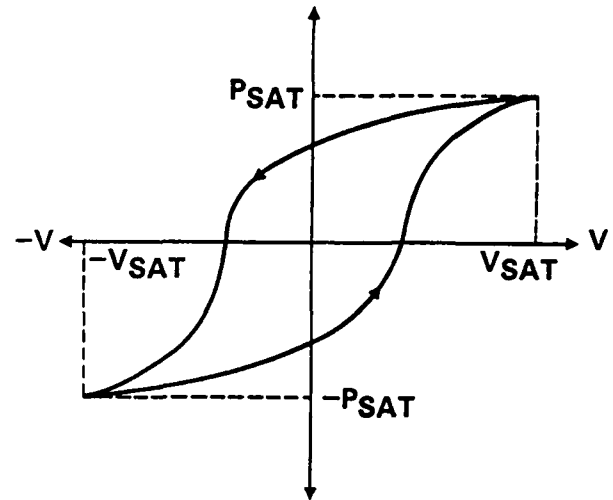


FIGURE 1

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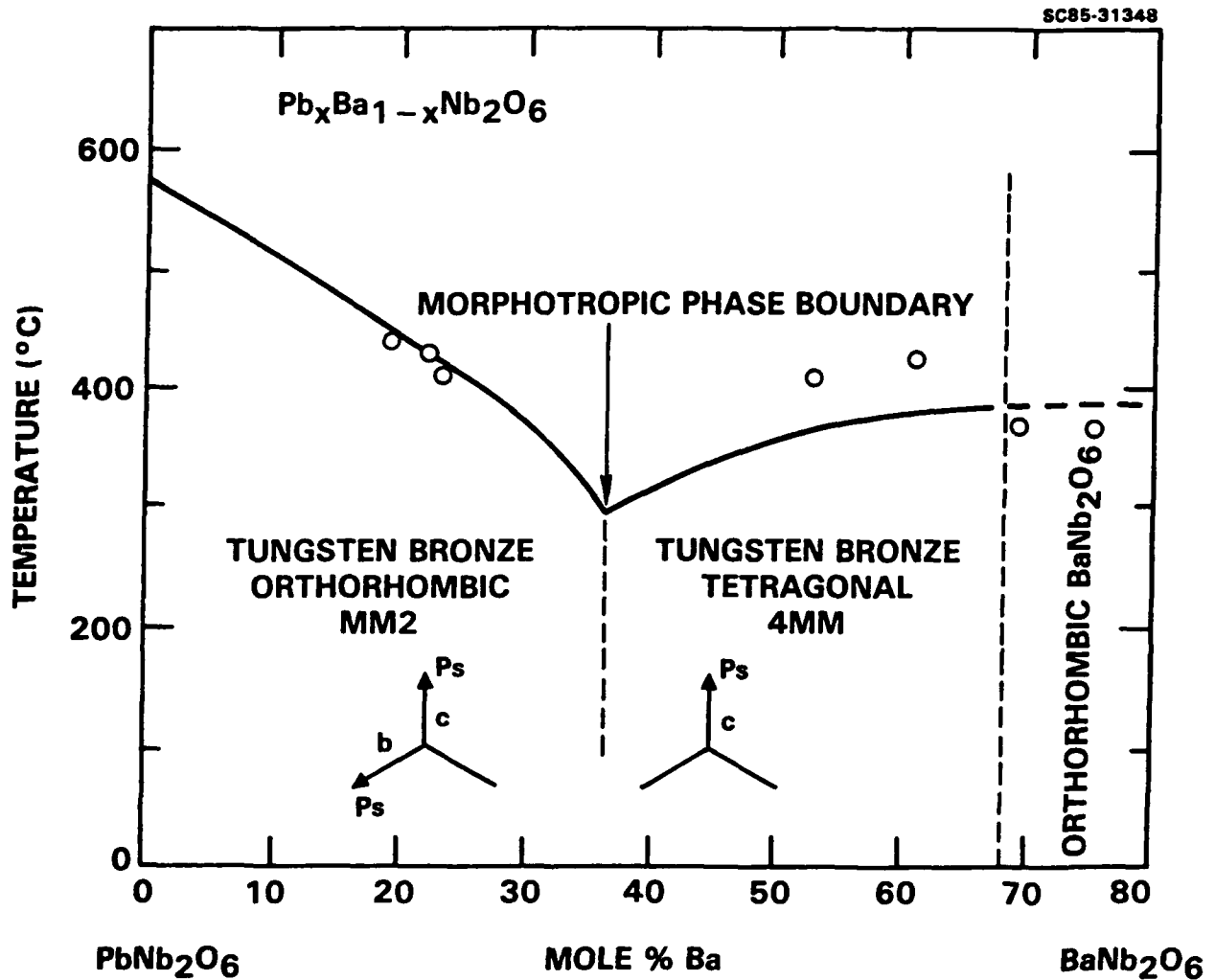
IDEAL REQUIREMENT



OBSERVED BEHAVIOR



FIGURE 2



THE PSEUDO-BINARY PbNb_2O_6 - BaNb_2O_6 SYSTEM



FIGURE 3

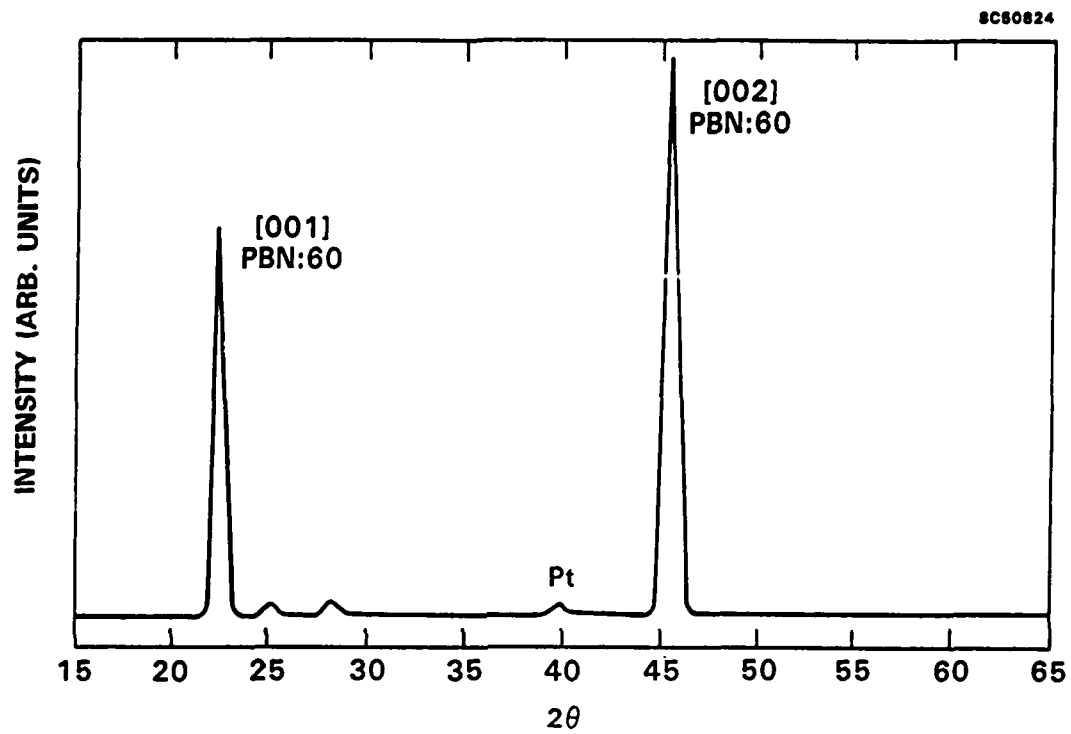




FIGURE 4

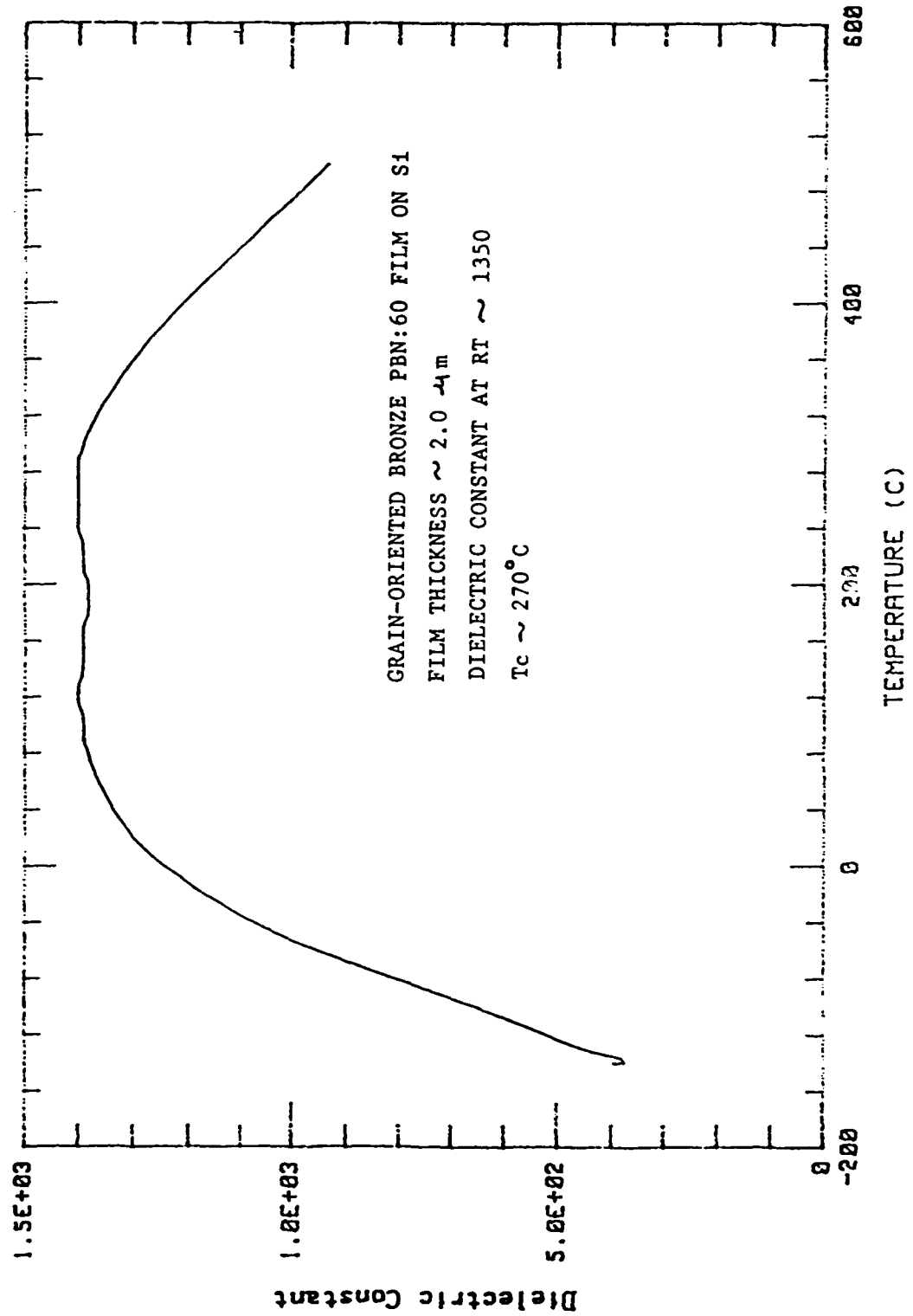




FIGURE 5

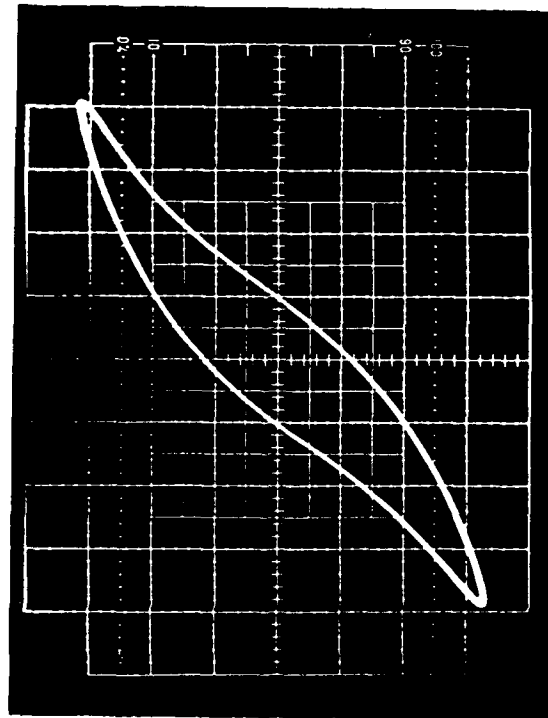
Film Thickness: 4.0 μm

Horizontal: 10 V / div.

Vertical: 5 $\mu\text{col} / \text{cm}^2 / \text{div.}$

Frequency: 60 Hz

Low Pinhole Density





EPITAXIAL GROWTH OF PLZT SINGLE CRYSTAL FILMS ON BRONZE SBN
SUBSTRATES BY THE SPUTTERING TECHNIQUE

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ABSTRACT

This paper reports the preliminary results of epitaxial growth of single crystal PLZT thin films on tungsten bronze $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (SBN:60) substrates by the rf sputtering technique. The films were deposited primarily with (100) SBN substrate orientation and temperatures over 500°C. These films exhibit excellent epitaxy with film orientation along the (100) direction. A multilayer approach has been proposed to improve film quality and properties.



INTRODUCTION

A lanthanum-modified lead-zirconate-titanate solid solution system (PLZT) is a well known ferroelectric material. PLZT is transparent in the visible and near-infrared regions, has various electro-optic¹ and photochromic² activities, and promises excellent optoelectronic properties. There have been numerous concepts for its application in electronic and optoelectronic devices making use of these interesting properties, e.g., in a nonvolatile FET memory with ferroelectric gates;^{3,4} optical switches;⁵ image storage;⁶ optical modulators;⁷ and, optical display devices.⁸ Considerable practical interest has been generated on a PLZT thin films for the purpose of reducing the drive voltage, miniaturization and cost reduction of optoelectronic devices.

Quite recently, several attempts to prepare a PLZT thin films have been initiated using rf sputtering and electron beam evaporation,⁹⁻¹³ and some PLZT thin films possessing good ferroelectric properties have been obtained. However, from the viewpoint of applications in optical waveguide systems, the preparation of better thin films with high transparency is required. The most significant obstacle in obtaining good transparency and electro-optic properties is the difficulty in growing the perovskite structure with large grain size on suitable substrate materials during film deposition and heat treatment, since the grains increase absorption due to light scattering. We have conducted a series of experiments on the epitaxial growth of PLZT thin films on single crystal tungsten bronze $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (SBN:60) substrates and have succeeded in growing these films with good crystallinity. In this paper, the growth of these thin films, their structural properties, and their applicability to electro-optic devices in integrated optics are discussed.



Experimental Procedure

The sputtering targets employed were a mixture of PLZT and PbO. Approximately 5 mole% excess of PbO was added in the targets to control the Pb^{2+} concentration in the films. The targets were prepared using ceramic sintering or hot-pressing; well-mixed powders were cold pressed and then sintered or hot-pressed at 1000°C after ball-milling. The Zr:Ti ratio was 45:55 and the La^{3+} concentration varied between 2 to 5 mole% in these targets. The targets thus prepared showed no extra phases and were fabricated in 3 in. diameters to obtain uniform film deposition.

The PLZT thin films were deposited with an MRC rf sputtering instrument; the sputtering conditions are summarized in Table I. SBN:60 crystal substrates of dimensions $10 \times 10 \times 1$ mm were cut in the (001) plane. Some of the substrates were polished to optical quality, etched with HF acid after polishing, or mechanochemically polished. The substrate temperature was maintained between 100 to 500°C during these film growths.

RESULTS AND DISCUSSION

The epitaxial growth of PZT and PLZT has been subject of great interest for various applications, with film growth proving successful on various substrates (MgO, Si, SiO_2 , Al_2O_3 , Pt, glass, etc.). However, the films obtained on these substrates are basically polycrystalline, with frequent occurrences of a pyrochlore phase. Recently, Higuma et al.^{14,15} grew PLZT films on SrTiO_3 substrates and reported that the films were single crystal with excellent epitaxy. SrTiO_3 is cubic at room temperature with a lattice constant $a = 3.905\text{\AA}$, while PLZT can be either rhombohedral or tetragonal, depending upon the Zr:Ti ratio. The lattice constants for the tetragonal PLZT solid solution are $a = 3.904$ to 4.05\AA .



and $c = 4.05$ to 4.15\AA . Thus, one can adjust the film composition such that there is a good lattice match with the substrate. In the present work, we have employed tungsten bronze SBN:60 substrates which are tetragonal at room temperature with lattice constants $a = 12.468\text{\AA}$ and $c = 3.938\text{\AA}$.¹⁶ The PLZT composition selected for epitaxial growth was $\text{Pb}_{0.97}\text{La}_{0.03}\text{Zr}_{0.45}\text{Ti}_{0.55}\text{O}_3$ (3/45/55) with lattice constants $a = 3.955\text{\AA}$ and $c = 4.125\text{\AA}$. This composition has an excellent lattice match with SBN:60 substrates in the following two orientations:

$$(100)_{\text{film}} = (001)_{\text{sub.}} \quad [a_{\text{film}} = c_{\text{sub}}]$$

$$3 \times (001)_{\text{film}} = (100)_{\text{sub.}} \quad [3 \times c_{\text{film}} = a_{\text{sub}}]$$

As shown in Fig. 1, 3 cm diameter, 7 cm long SBN:60 single crystals of optical quality were used in these growths.^{17,18} Two other tungsten bronze crystals having slightly bigger lattice constants, SBN:50 and BSKNN-1, are also available for use as substrates.

PLZT thin films were deposited on (001)-oriented SBN:60 with substrate temperatures varied between 100 and 500°C. As summarized in Table I, all films were grown in an Ar:O₂ atmosphere. The sputtering conditions were as follows:

Target-Substrate Distance:	4-5 cm
Input Power Density:	1.9 to 2.4 W/cm ²
Gas Mixture:	Ar:O ₂ (50:50)
Substrate Temperature:	100 to 500°C
Deposition Rate:	50-100Å/hr
Annealing Temperature:	600-650°C



Figure 2 shows x-ray diffraction patterns of PLZT thin films deposited on glass and SBN:60 substrates and annealed at 600°C. All of the tetragonal perovskite peaks of PLZT were observed when the film was deposited on glass, with the formation of the pyrochlore phase below 600°C. This result is consistent with work reported by various researchers, including our earlier work.^{5-15,19} However, when the film was deposited on the (001)-oriented SBN:60 substrates, only the (100) and (200) diffraction peaks of the film were observed. This clearly shows that the PLZT films deposited on SBN substrates are single crystal with excellent epitaxy. We believe that this is the first time such perovskite films have been grown on tungsten bronze substrates.

The growth of PLZT films was investigated at various substrate temperatures and it was found that the films grown below 400°C were weakly crystallized and needed subsequent annealing above 500°C. However, films grown at substrate temperatures of 500°C or above were well crystallized, single crystal films. Furthermore, the use of SBN substrates completely suppressed the formation of the pyrochlore PLZT phase even at lower temperatures. On the other hand, PLZT films grown on other substrates such as glass, Pt, Al₂O₃ and quartz always exhibited a pyrochlore phase and required high-temperature annealing to convert to the perovskite phase.

The occurrence of a pyrochlore phase is a subject of great interest in Pb²⁺-containing perovskites and it usually appears when the unit cell c/a ratio is below 1.06, as shown in Fig. 3. Since c/a for PbTiO₃-BiFeO₃ is 1.17, one does not observe the pyrochlore phase on this system. On the other hand, the pyrochlore phase is found for all compositions in the PbTiO₃-PbZn_{0.33}Nb_{0.66}O₃ system. The latter is exceptionally important for electro-optic and piezoelectric applications because it exhibits both electro-optic and piezoelectric coefficients very large with a large spontaneous polarization.



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The lattice constant a is estimated to be 3.955\AA in the PLZT films, in close agreement with the ceramic target value. Electron diffraction patterns need to be studied to ascertain the single crystallinity and polar direction in these films. PLZT deposited on SBN:60 substrates are completely transparent in the visible, cutting off in the IR because of substrate absorption. According to work by Okuyama et al,¹⁵ PLZT films deposited on MgO and SrTiO₃ are transparent from the visible to the near-IR. Optical measurements on their films suggest that the optical loss is about 6 db/cm, which is slightly higher than that of LiTaO₃ single crystals. However, the half-wave voltage is about one fortieth of that for LiNbO₃, and the reduction of the element size would compensate for the large loss factor. We suspect that this loss can be suppressed further by using well matched substrates such as SBN:60 or other bronze materials.

FUTURE PLANNED WORK: MULTILAYER THIN FILMS

Since the growth of single crystal PLZT thin films on SBN:60 has been successful, it opens up various ways one can improve film quality. If the optical quality or optical loss remains a problem for device applications, a multilayer approach may be appropriate for these films. Since tungsten bronze $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (PBN:60) has a c lattice constant close to the a constant of PLZT, a possibility is to first deposit a PBN:L60 layer on an SBN:60 substrate and then deposit the PLZT film on this layer. Figure 4 summarizes our experimental approach for this concept. As shown in the figure, additional layers of PBN:60 and PLZT may be deposited to improve the film quality of the final film layer. For spatial light modulators and guided wave optics, it is advantageous for the films to have an optical refractive index larger than the substrate, while still maintaining a large optical figure-of-



merit, r_{ij}/ϵ . As shown in Fig. 4, PLZT possesses a significantly larger index than tungsten bronze materials, with Δn of around 0.10.

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FIGURE CAPTIONS

Fig. 1 SBN:60 single crystals grown along $\langle 001 \rangle$.

Fig. 2 Perovskite PLZT thin films on tungsten bronze SBN:60 substrate.

Fig. 3 The c/a ratio for perovskite materials.

Fig. 4 Advantages of multilayer ferroelectric thin films.



Table 1
Growth of PLZT Thin Films on SBN Substrates

PLZT Film	Lattice-Match	As-Grown	Annealed Above 600°C	Lattice Constant	Remarks
(001)-oriented SBN:60 (substrate)					
≤ 400°C	0.40%	Weakly crystallized	Single crystal film	3.953Å	Excellent quality
≥ 550°C	0.40%	Well crystallized	Single crystal film	3.957Å	Excellent quality
Glass-Substrate					
≤ 400°C	--	Amorphous	<600°C pyrochlore >500°C perovskite	a = 3.961Å	Pyrochlore phase problem
≥ 550°C	--	Weakly crystallized pyrochlore	600°C perovskite (polycrystalline)	c = 4.121Å	

Lattice Constants: SBN:60 a = 12.458Å, c = 3.938Å
PLZT a = 3.955Å, c = 4.125Å



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FIGURE 1

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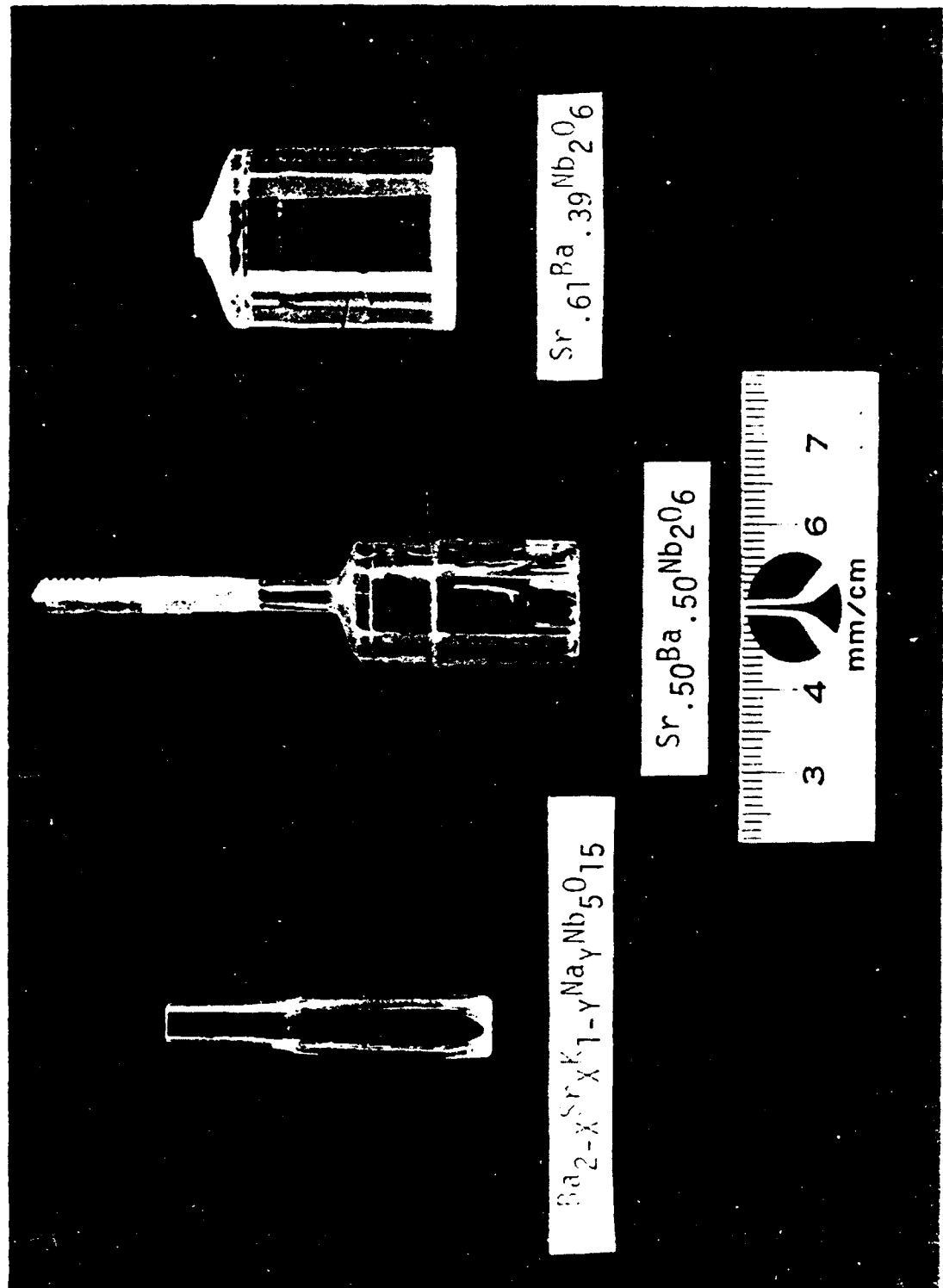
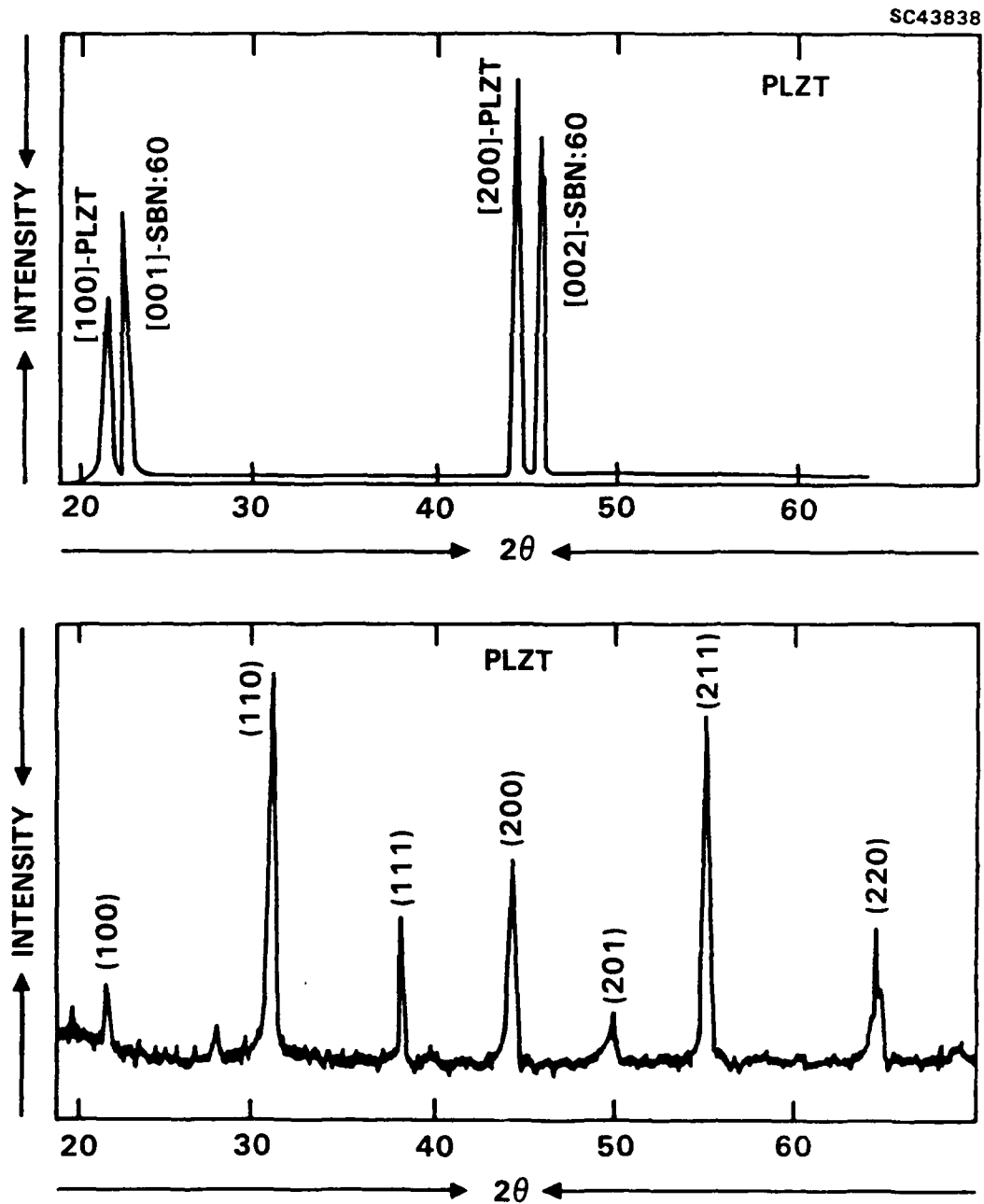




FIGURE 2

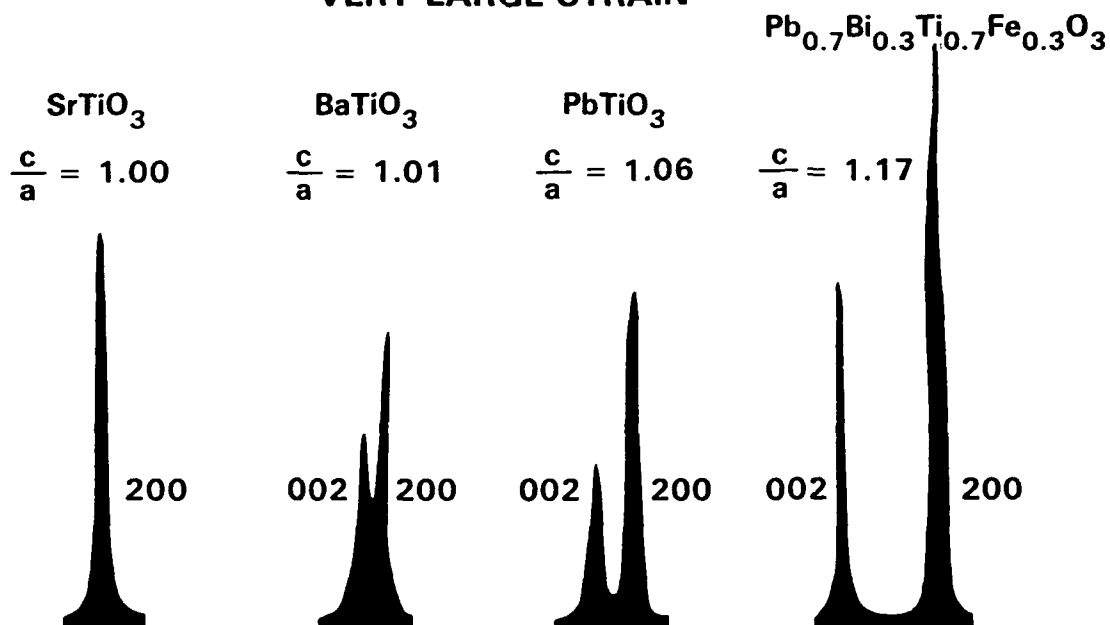
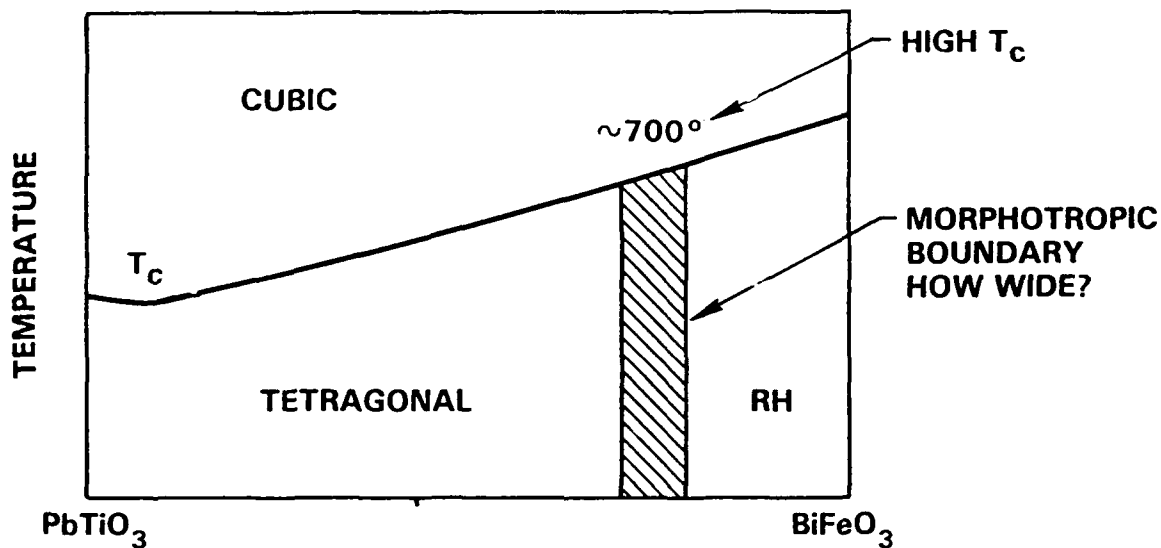




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FIGURE 3

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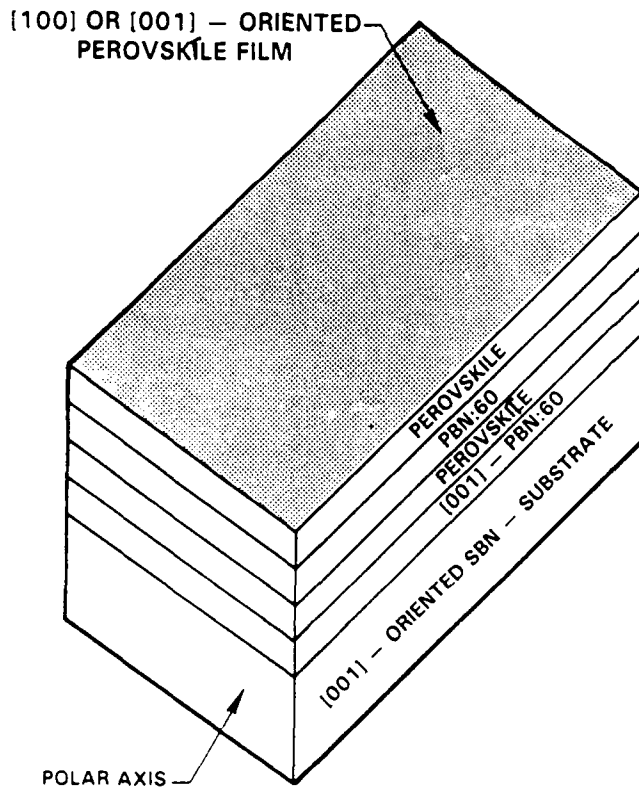


X-RAY (200) PEAKS



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FIGURE 4



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SBN:60

PBN:60

PEROVSKITES

[001]

[001]

[100] OR [001]

$n = 2.24$

$n = 2.32$

$n = 2.4$ TO 2.76

LARGE r_{33} , ϵ_{33}

LARGE r_{51} , ϵ_{11}

LARGE r_{51} , ϵ_{33}

$T_c = 78^\circ\text{C}$

$T_c = 280^\circ\text{C}$

$T_c = 100 - 300^\circ\text{C}$

PEROVSKITE FILMS

PZT, PLZT, PZNT, PBFT

APPLICATIONS

- OPTICAL WAVEGUIDES AND SWITCHES
- 3-D STORAGE AND DISPLAY
- PYROELECTRIC AND PIEZOELECTRIC
- MULTILAYER CAPACITORS



GROWTH OF PEROVSKITE PZT AND PLZT THIN FILMS

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ABSTRACT

This paper reports preliminary results on the fabrication of perovskite PZT and PLZT thin films using a sputtering technique. For glass, quartz and sapphire substrates, it was necessary to raise the substrate temperature above 550°C to achieve perovskite tetragonal structures of interest. Growth at temperatures below 550°C yielded a major pyrochlore structure phase. Excess of PbO in target was also required to maintain stoichiometry in these films.



INTRODUCTION

Recently, considerable attention has focused on the development of low-loss ferroelectric thin films for optical waveguides. Several attempts have been made to grow single crystal waveguide films using materials such as LiNbO_3 ,¹⁻³ PLZT,⁴⁻⁶ KLN and SBN.^{7,8} More recently, other ferroelectric materials such as BaTiO_3 and PBN have been considered using semiconductor substrates for various optical applications, including waveguides, spatial light modulators, switches and pyroelectric detectors. The top surfaces of as-grown LiNbO_3 and SBN films fabricated by liquid phase epitaxial growth, chemical vapor deposition, melting methods and so on, are relatively rough so that they must be optically polished to couple a light beam into the film. On the other hand, polishing is not necessary for sputtered thin films. Therefore, the sputtering technique has been used in the present work to develop perovskite PZT and PLZT films using a variety of substrates such as glass, quartz and sapphire. This paper reports the growth of PZT and PLZT films and their associated growth problems.

EXPERIMENTAL PROCEDURE

The sputtering targets employed were a mixture of PZT or PLZT and PbO . Approximately 5 mole% excess PbO was added in these targets to control the Pb concentration in the films. The targets were prepared using ceramic sintering or hot pressing; well-mixed powders were cold pressed and then sintered or hot pressed at 1100°C after ball-milling.



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Sapphire (Al_2O_3) and quartz (SiO_2) substrates were first etched by sputtering. The substrates were mounted on a heating block with a stainless steel mask of 0.2 mm thickness. Substrate temperature was monitored by a Pt-Pt.Rh 13% thermocouple inserted into the center of the substrate holder. The sputtering conditions, summarized in Table 1 for each material, are as follows:

Target-Substrate Distance:	5 cm
Input Power Density	1.9 to 2.4 W/cm^2
Sputtering Gas	$\text{Ar}:\text{O}_2$ (40:60 or 50:50)
Gas Pressure	8-12 μm
Substrate Temperature	300-600°C
Deposition Rate	20-25 Å/h
Annealing Temperature	700-800°C

EXPERIMENTAL RESULTS AND DISCUSSION

PZT and PLZT compositions have been of practical interest for the last 25 years and are being exploited for optical applications such as switches, modulators, image storage and optical display devices. PZT occurs on the pseudobinary PbZrO_3 - PbTiO_3 system and exhibits a morphotropic phase boundary at a Zr:Ti ratio of 52:48, as shown in Fig. 1. However, the development of bulk single crystals has been hindered by growth problems associated with Pb^{2+} losses during growth and cracking when cycling through the paraelectric/ferroelectric phase transition. For this reason, thin-film growth of these compositions is now being explored in several countries.⁹⁻¹¹



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The deposition of PZT and PLZT films by the sputtering technique has shown that the structure of the film is sensitive to the substrate temperature (Fig. 2). PZT or PLZT thin films having a pyrochlore structure were obtained below 550°C, whereas a perovskite structure was obtained above 600°C. However, traces of PbTi_3O_7 were observed with Pb^{2+} deficiencies, and for this reason, an extra 5 mole% PbO was incorporated in the targets to stabilize the film composition.

Figure 3 shows the x-ray diffraction patterns of PLZT films sputtered on fused quartz and sapphire and for a PLZT(9/65/35) hot-pressed ceramic. In Fig. 3, (a) is for a film (~ 4 μm thickness) sputtered at a substrate temperature of 550°C with a target containing 5 mole% of PbO excess, (b) is for a film sputtered at 600°C with a target containing 3 mole% PbO excess, and (c) is for the hot-pressed PLZT ceramic target. The good agreement between the thin film and ceramic target patterns shows that the films have maintained the desired perovskite structure, although they are polycrystalline due to the poor lattice match with the substrates. A small split of the (200) peak into (200) and (002) was observed after a post-growth anneal at 700°C/2 h, indicating a tetragonal symmetry. However, this caused some loss of Pb^{2+} , as indicated by the appearance of small second phase peaks associated with ZrO_2 . To maintain a perovskite phase during growth, substrates were held at 600–650°C; growth temperatures below 350°C resulted in completely amorphous films which could not be annealed to a crystalline form. Although excess PbO is clearly required to maintain film stoichiometry during growth, based on evidence from this work and the results of others,¹ the optimum excess PbO amount still needs to be established.



FUTURE PLANNED WORK: MULTILAYERED FERROELECTRIC FILMS

Recent work by Higuma et al¹² has shown that the growth of PLZT single crystal films is possible using perovskite SrTiO_3 substrates at temperatures between 500 and 700°C. Although film growth was successful, there was a considerable lattice mismatch between the film and the substrate. Table 2 summarizes the lattice match of PLZT with SrTiO_3 and other ferroelectric crystals, including tungsten bronze SBN and PBN. The lattice match between PLZT and PBN is very good for (001)-oriented PBN and potentially allows the growth of better quality PLZT films. In future work, we propose to develop PZT and PLZT films as follows:

1. SBN:60 substrate with a 5 μm PBN:60 film for lattice matching to PZT or PLZT.
2. SBN:60 substrate with a 5 μm PBN:60 film and then alternate PLZT and PBN layers to develop a superlattice structure.

Since the lattice mismatch between PLZT and PBN is small, we expect that optical-quality PZT/PLZT films or PLZT-PBN superlattices can be more readily achieved with these film structures. An additional advantage is the ability to improve the lattice match by adjustment of the Pb:Ba ratio in PBN and thereby improve PZT/PLZT film crystallinity.

The previously discussed considerations for the electrical evaluation of PBN:60 thin films also apply here in the case of PZT/PLZT films. Because of the additional complexity of PZT/PLZT thin-film growth, the growth of good



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quality films on metallized substrates may be vastly more difficult than for PBN:60. A closely spaced surface electrode configuration appears to be a preferable geometry for electrical characterization of PZT/PLZT films, at least in the near term. A high-temperature sample holder to accommodate this type of geometry for dc conductivity, pyroelectric and dielectric measurements over a wide temperature range is now being designed and tested for this purpose.

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FIGURE CAPTIONS

- Fig. 1 Morphotropic phase boundary in the PZT system.
- Fig. 2 Structural sensitivity of PZT and PLZT compositions.
- Fig. 3 X-ray diffraction patterns of PLZT sputtered films and hot-pressed ceramic. (a) Film sputtered with a target with 5 mole% excess PbO; (b) film sputtered with a target with 3 mole% excess PbO; and (c) hot-pressed ceramic.



Table 1
Growth Condition for PZT and PLZT Films

Substrate	Substrate Temperature ≤ 550°C	Substrate Temperature ~ 600°C	Atmosphere	Power Density (W/cm ²)	Film Thickness (μm)	Remarks
PZT Films						
Glass	Pyrochlore	Perovskite	50% Ar + 50% O ₂	2.2-2.4	1-5	Excellent Films Reasonable Quality
Quartz (SiO ₂)	Pyrochlore	Perovskite	50% Ar + 50% O ₂	2.2-2.4	3-10	
Sapphire (Al ₂ O ₃)	Pyrochlore	Perovskite	50% Ar + 50% O ₂	2.2-2.4	3-10	
PLZT Films						
Glass	Pyrochlore	Perovskite	40% Ar + 60% O ₂	1.9-2.1	3-10	Reasonable Quality
Quartz (SiO ₂)	Pyrochlore	Perovskite	40% Ar + 60% O ₂	1.9-2.1	2-8	Excellent Quality
Sapphire (Al ₂ C ₃)	Pyrochlore	Perovskite	40% Ar + 60% O ₂	1.9-2.1	2-5	Reasonable Quality

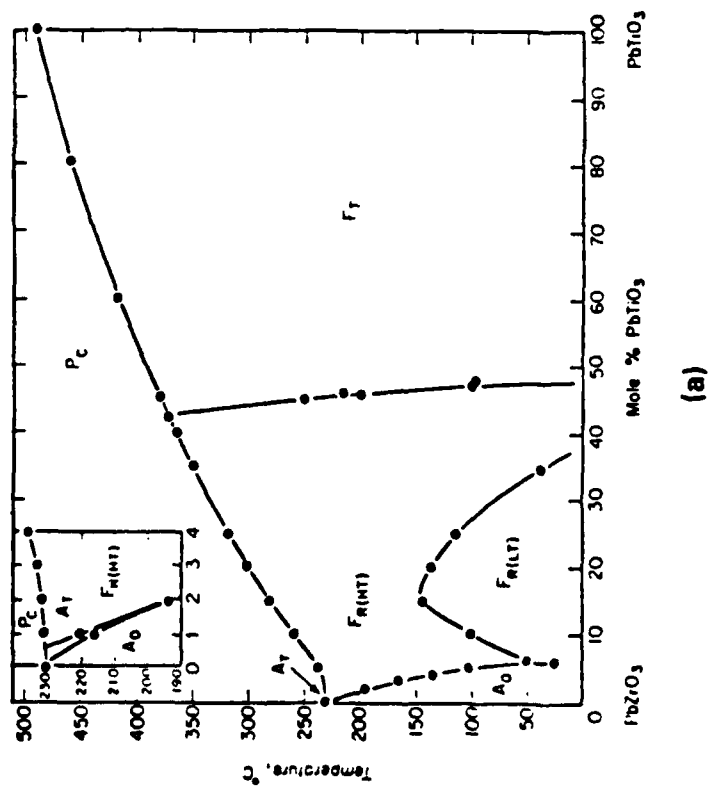
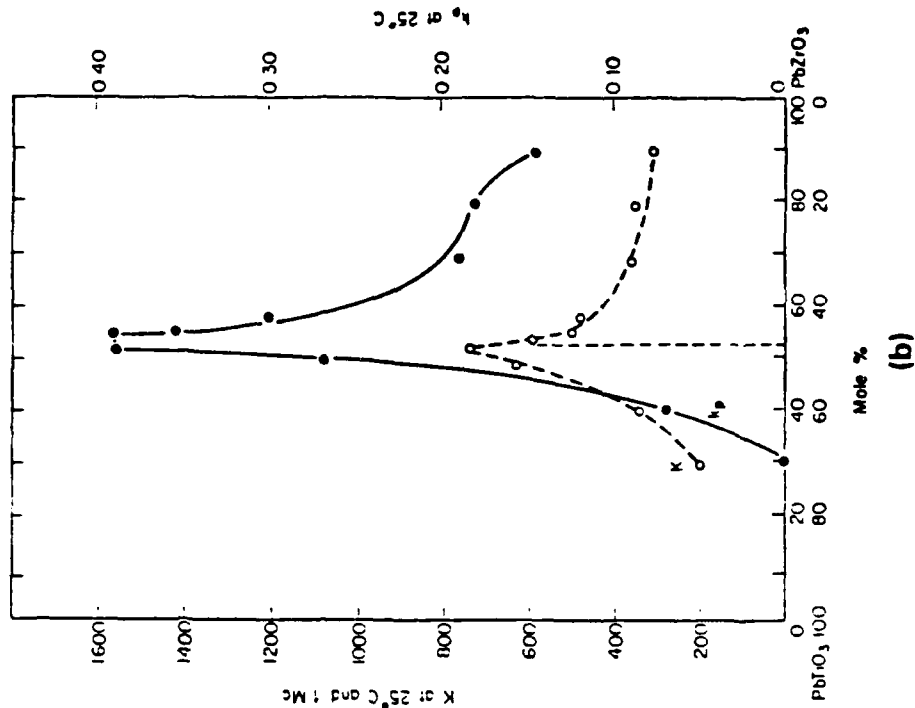


Table 2
Lattice Match Between PZT/PLZT and Tungsten Bronze Substrates

Film Composition	(001)-Oriented Tungsten Bronze Substrates			Perovskite
	SBN:60	BSKNN	PBN:60	SrTiO ₃
<u>PZT (40:60)</u>				
a = 4.042Å	2.6%	1.99%	1.4%	3.01%
c = 4.082Å	3.6%	3.00%	3.00%	4.12%
<u>PLZT (8/40/60)</u>				
a = 4.029Å	2.1%	1.5%	1.1%	2.5%
c = 4.072Å	3.4%	2.7%	2.1%	4.3%
<u>PBN:60</u>				
a = 12.501Å	0.38%	0.20%	-----	-----
c = 3.985Å	0.65%	0.35%	-----	-----

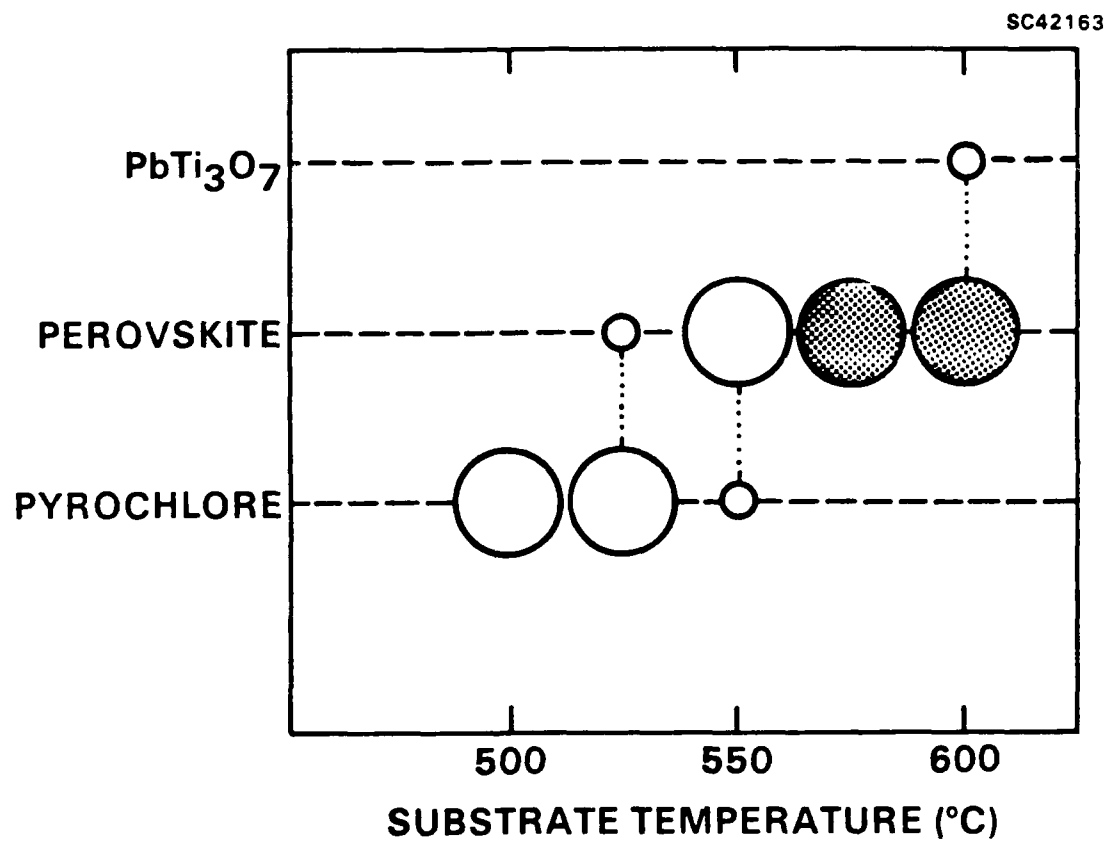


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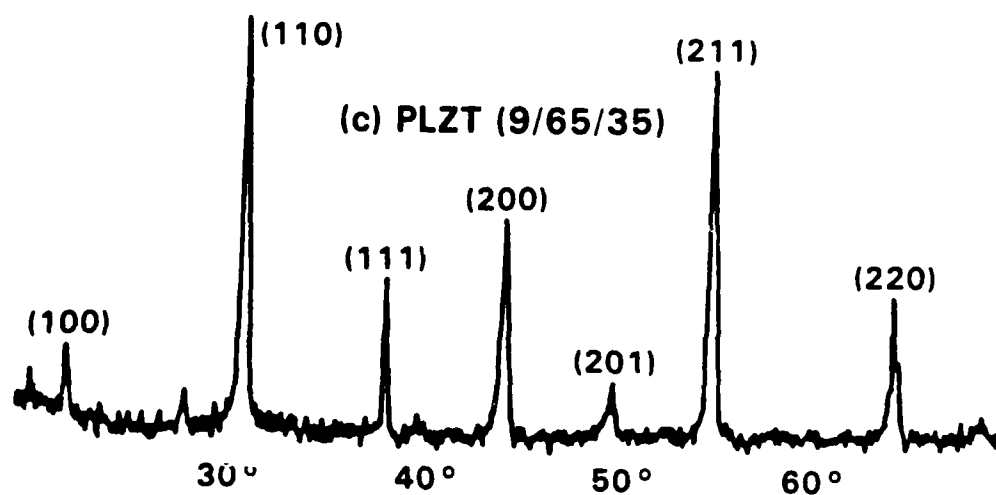
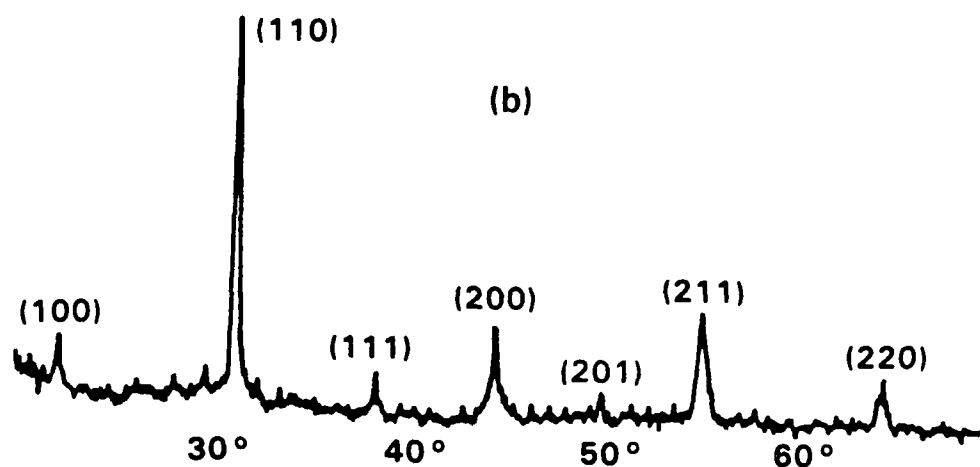
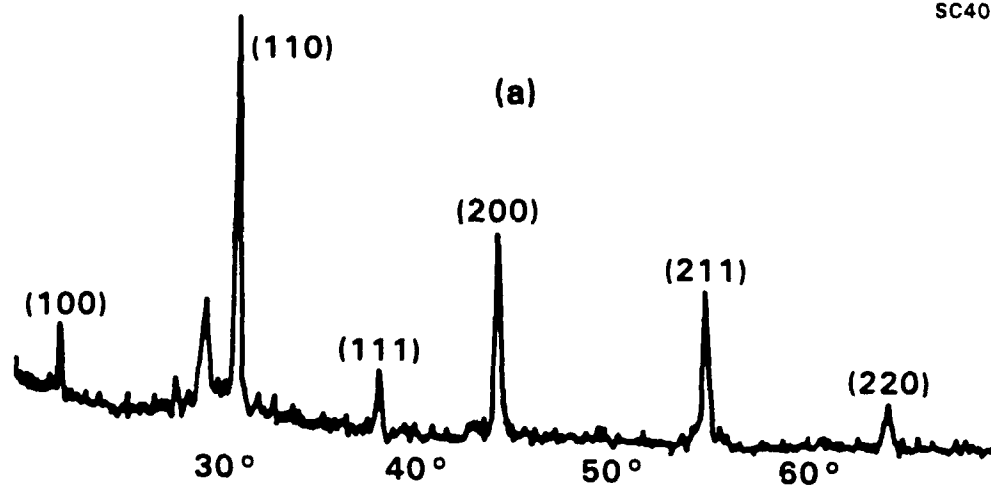


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Magnetron sputtering, ferroelectric thin films, PBN:60, SBN:75
PZR/PLZT, lattice-matched substrates, electro-optics

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The magnetron sputtering technique has been used to grow morphotropic phase boundary ferroelectric thin films of tungsten bronze PBN:60 and perovskite PLZT. Film crystallinity was found to be strongly influenced by substrate temperature, with temperatures of 500-600°C usually required. Single crystal PBN:60 films were grown on SBN:60 substrates, whereas grain-oriented films were achieved on (100)-oriented Si substrates. PLZT films are grain-oriented for (001)-oriented SBN and have excellent surface quality for guided wave applications. This is the first time such films have been grown on tungsten bronze substrates. Both PBN:60 and PLZT films present a great promise for SLM and electronic memory applications.

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